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ADSORPTION OF Pb^{2+}, Cu^{2+} AND Co^{2+} BY POLYPROPYLENE FABRIC AND POLYETHYLENE HOLLOW FIBER MODIFIED BY RADIATION-INDUCED GRAFT COPOLYMERIZATION

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Abstract–Cation-exchange adsorbents were prepared by radiation-induced grafting of glycidyl methacrylate (GMA) onto polypropylene (PP) fabric and polyethylene (PE) hollow fiber and subsequent phosphonation of epoxy groups of poly(GMA) graft chains. The adsorption characteristics of Pb^{2+}, Cu^{2+} and Co^{2+} for the two cation-exchange adsorbents were studied. In the grafting of GMA onto PP fabric, the degree of grafting (%) increased with an increase in reaction time, reaction temperature, and pre-irradiation dose. The maximum grafting yield was observed around 60 % GMA concentration. In 50, 130 and 250 % GMA-grafted PP fabric, the content of phosphoric acid was 1.52, 3.40 and 4.50 mmol/g at 80 °C in the 85 % phosphoric acid aqueous solution for 24 h, respectively. The adsorption of Pb^{2+}, Cu^{2+} and Co^{2+} by PP fabric adsorbent was enhanced with an increased phosphoric acid content. The order of adsorption capacity of the PP fabric adsorbent was $Pb^{2+}>Co^{2+}>Cu^{2+}$. In adsorption of Pb^{2+}, Cu^{2+} and Co^{2+} by PE hollow fiber, the amount of Pb^{2+} adsorbed by the PE hollow fiber adsorbent containing 1.21 mmol/g of $-PO_3H$ was *ca.* 54.4 g per kg. The adsorption amount of Cu^{2+} and Co^{2+} in the same PE hollow fiber was *ca.* 21.0 g per kg and *ca.* 32.1 g per kg, respectively. The order of adsorption of the PE hollow fiber adsorbent was $Pb^{2+}>Co^{2+}>Cu^{2+}$.

Key words : Radiation-Induced Graft Copolymerization, Polypropylene Fabric, Polyethylene Hollow Fiber

INTRODUCTION

Graft polymerization of vinyl monomer onto the polymer substrates has attracted considerable interest because it imparts some desirable properties such as biocompatibility [Wilke et al., 1998; Kamath et al., 1994], ion exchange [Sata, 1996; Soulier et al., 1998] and protein adsorption [Ishihara et al., 1998].

Graft polymerization is achieved by ionization radiation [Kim et al., 1996], UV [Dauphin, 1994; Matsui et al., 1998] or plasma [Kang et al., 1993]. However, among them radiation-induced grafting can be one of the most effective techniques because of its uniform creation of radical sites in the polymer matrix. In general, two techniques for radiation-grafting can be employed : (1) by the direct method, where a polymer substrate is immersed or dissolved in either an individual monomer or a solution of monomers and then the whole mixture is irradiated, and (2) by the pre-irradiation method, where a polymer substrate is activated by irradiation regardless of the presence of oxygen, and sequentially allowed to react with the monomer.

Graft polymerization of GMA onto polymer substrates is advantageous because the epoxy group of GMA is modified easily to have functions such as ion exchange and chelating [Choi et al., 1998] with the original properties remaining intact.

In our previous studies [Choi et al., 1998], the cation-exchange hollow fiber membrane (CEM) was prepared by radiation-induced grafting of GMA onto a polyethylene hollow fiber membrane and its sulfonation. When the Pb^{2+} and Co^{2+} solution was permeated across the CEM with the $-SO_3H$, the adsorption characteristics of Pb^{2+} and Co^{2+} on the CEM were examined.

In this study, two cation-exchange adsorbents were prepared by radiation-induced graft of GMA onto polypropylene (PP) fabric and polyethylene (PE) hollow fiber, and subsequent phosphonation of epoxy groups of poly(GMA) graft chains. When Pb^{2+}, Cu^{2+} and Co^{2+} were adsorbed by the PP fabric and were permeated across PE hollow fiber, the adsorption characteristics of the two cation-exchange adsorbents containing phosphoric acid for Pb^{2+}, Cu^{2+} and Co^{2+} were studied.

EXPERIMENTAL

1. Materials

Commercial PP fabrics of 140 g/m² (Chongbang Industries Co.) were washed with methanol and dried in a vacuum oven at 50 °C for 6 h. A commercially available microfiltration hollow fiber (Ashahi Chemical Industry Co., Ltd.) was used as a trunk polymer for the grafting. The inner and outer diameters of porous PE hollow fiber were 1.95 and 3.01 mm, respectively. PE hollow fiber has 0.34 μm pore diameter and 71 % porosity. Cupric chloride ($CuCl_2 \cdot 2H_2O$) and cobalt chlorade hexahydrate ($CoCl_2 \cdot 6H_2O$) were obtained from Junsei Chemical Co., Ltd. Glycidyl methacrylate [$CH_2=C(CH_3)COOCH_2CHOCH_2$, GMA] was used without further purification. Other chemicals were reagent grade.

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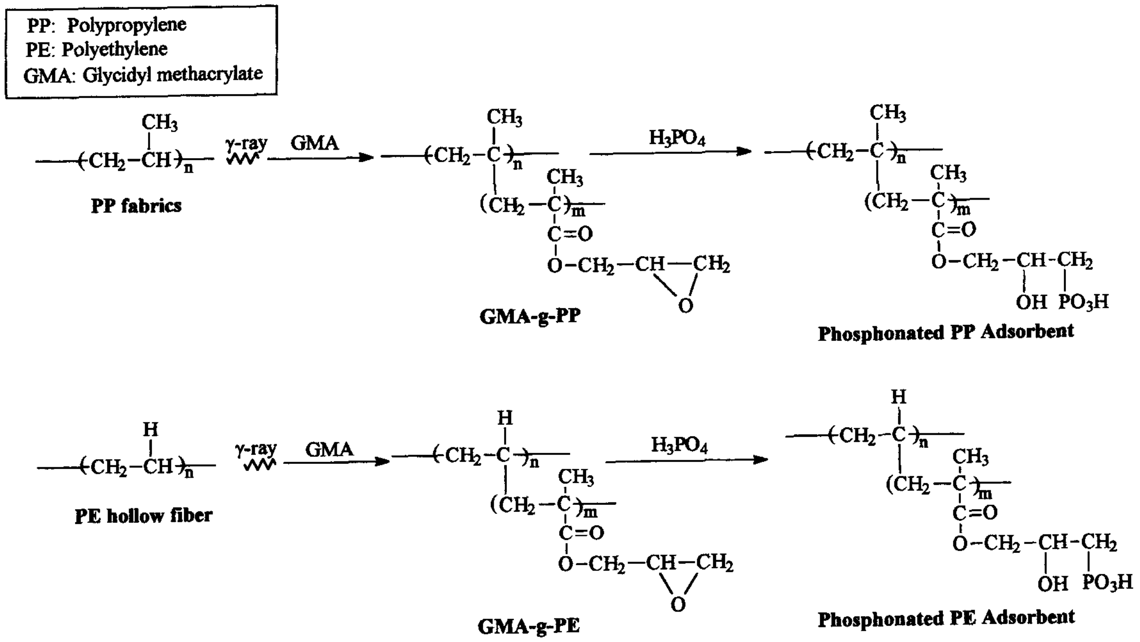


Scheme I. Preparation of two cation-exchange adsorbents.

2. Grafting Procedure

Scheme I shows the preparation procedure of radiation grafting of GMA onto PP fabrics and PE hollow fiber. The PP fabrics and PE hollow fiber were used as the base polymer for grafting polymerization. The base polymer was irradiated by γ-ray from Co-60 under atmospheric pressure and ambient temperature, then immediately the irradiated PP fabrics and PE hollow fiber were reacted with monomer. The unreacted monomer and homopolymers were removed after grafting with tetrahydrofurane (THF) using Soxhlet apparatus. The GMA-grafted PP fabrics and PE hollow fiber obtained by grafting copolymerization were dried in a vacuum oven at 60 °C for 12 h. For the studies of the effects of various parameters on the grafting copolymerization, the degree of grafting was defined as [Choi et al., 1998; Nho et al., 1997]

$$\text{Degree of grafting } (\%) = [(Wg-Wo)/Wo] \times 100 \qquad (1)$$

where Wg and Wo denote the weights of the grafted and the ungrafted PP fabric and PE hollow fiber, respectively.

3. Phosphonation Procedure

The resultant epoxy group was converted into a phosphoric acid ($-PO_3H$) group by immersing the GMA-grafted PP fabric and PE hollow fiber in 85 % phosphoric acid aqueous solution at 80 °C. Subsequently, the adsorbents were repeatedly washed with water. The phosphoric acid content (mmol/g) was determined by

$$\text{Phosphoric Acid Content (mmol/g)} = [(Ws-Wg)/Ws] \times (1000/81) \qquad (2)$$

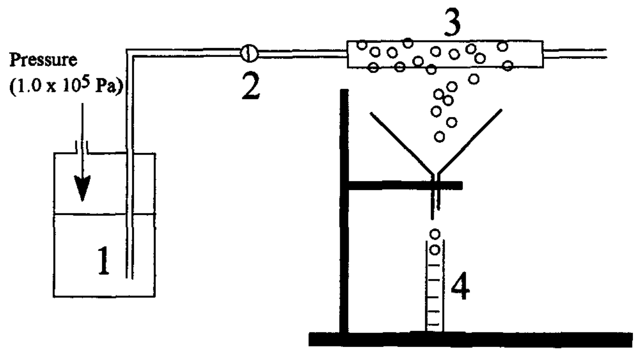
where Ws is the weight of the phosphonated PP fabrics and PE hollow fiber, and the factor of 81 corresponds to the molecular weights of $-PO_3H$. $-PO_3H$ group content was also determined from measurement of total ion-exchange capacity by titration. H-form adsorbents were immersed in a 5 % NaCl aqueous solution at room temperature for 24 h, and then the hydrogen ions liberated from the adsorbents were titrated in 0.025 N NaOH solution.

4. Adsorption of Cu^{2+}, Pb^{2+} and Co^{2+}

The amount of Pb^{2+}, Cu^{2+}, and Co^{2+} absorbed onto the PP fabric adsorbents was determined as follows. First, the initial molar concentrations of Pb^{2+}, Cu^{2+} and Co^{2+} were each set at 100 mg per liter (50 mL). After the adsorption of metallic ion to PP fabric (about 0.5 g) for 72 h, the PP fabric was taken out of the solution, and then the remaining solution concentration was determined by inductively coupled plasma atomic emission spectroscopy (ICP).

5. Breakthrough Curve

Scheme II shows the experimental apparatus for measuring pure water flux and breakthrough curves. The inner and outer diameters and lengths of PE hollow fiber were measured in the wet state with a microscope. After the PE hollow fiber was dried in a vacuum, the pore volume distribution was meas-



Scheme II. Experimental apparatus for determining flux and breakthrough curves.

1. Feed tank	3. PE hollow fiber membrane
2. Flow controller	4. Measuring cylinder

ured by a mercury intrusion method. The flux, U_t was determined by :

$$U_t=(\text{volumetric flow rate})/\pi D_tL \quad (3)$$

where D_t is the inner diameter and L is the length of the PE hollow fiber (10 cm). The volume flow rate of the pure water was measured from the amount dropping from the outside of the PE hollow fiber. The pressure in the feed tank, shown in Scheme II, was 1.0×10^5 Pa. The concentrations of Pb^{2+}, Cu^{2+} and Co^{2+} obtained during permeation were determined by ICP. The extent of adsorption was determined by a ratio of C to C^o, C^o being the initial concentration of Pb^{2+}, Cu^{2+} and Co^{2+}, before the permeation across PE hollow fiber, and C being their final concentration after the permeation. The permeation volume (PV) was determined by :

$$PV=\pi D_tL U_tt \quad (4)$$

where t is the time of permeation.

RESULTS AND DISCUSSION

1. Preparation and Characterization of PP Fabric Adsorbent, and Its Adsorption Characterization to Pb^{2+}, Cu^{2+} and Co^{2+}

The grafting of GMA onto PP fabrics was carried out by the pre-irradiation grafting technique. Now attention was paid to study the effects of the reaction time, reaction temperature, radiation dose, and monomer concentration on the extent of grafting.

The effects of GMA concentration and pre-irradiation dose on grafting onto PP fabrics at 70 °C in MeOH for 180 min are shown in Fig. 1. The maximum grafting yield (%) was observed around 60 % monomer concentration, presumably due to the Trommsdroff-type effect [Nho et al., 1997; Choi et al., 1998]. The pronounced maximum at a certain concentration of monomer can also be explained partially by an increased rate of swelling of the grafted layer in a reaction medium of this composition. The grafting yields were found to increase with increase in the pre-irradiation dose.

Fig. 2 shows the effects of reaction time and pre-irradiation dose on the grafting of GMA onto PP fabric at a reaction temperature of 70 °C. The grafting yield was found to increase with an increase in pre-irradiation dose and reaction time.

The effects of reaction temperature and reaction time on the grafting of GMA onto PP fabric of 30 °C, 50 °C, and 70 °C are shown in Fig. 3. The grafting yield at 70 °C was much higher than that at 50 °C, and the lowest grafting yield was at 30 °C. When PP fabrics were irradiated in air, the peroxides were formed. The radicals decomposed on heating was initiated the

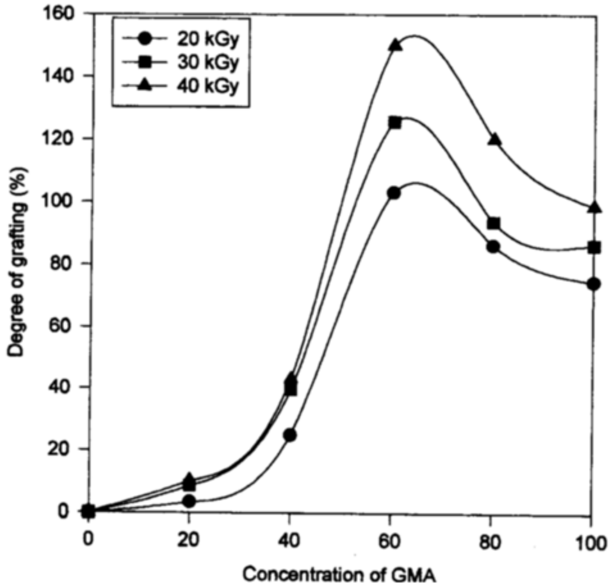


Fig. 1. Effect of GMA concentration on grafting onto PP fabrics ; reaction condition : 70 °C, 180 min.

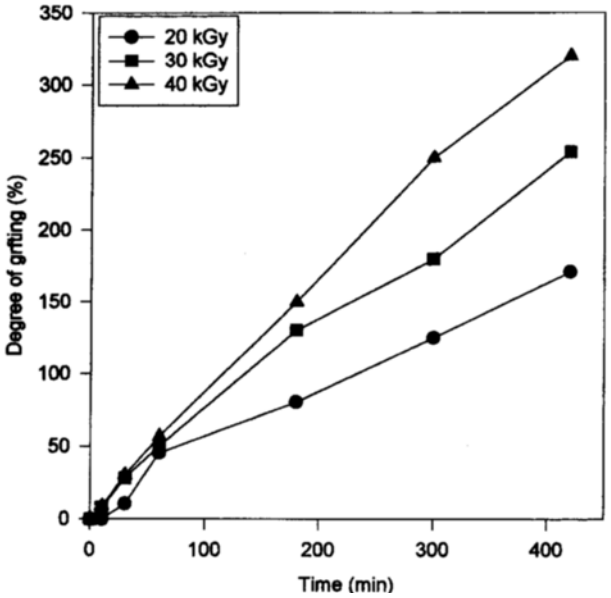


Fig. 2. Effect of reaction time on the grafting onto PP fabrics; reaction condition : 70 °C, in MeOH.

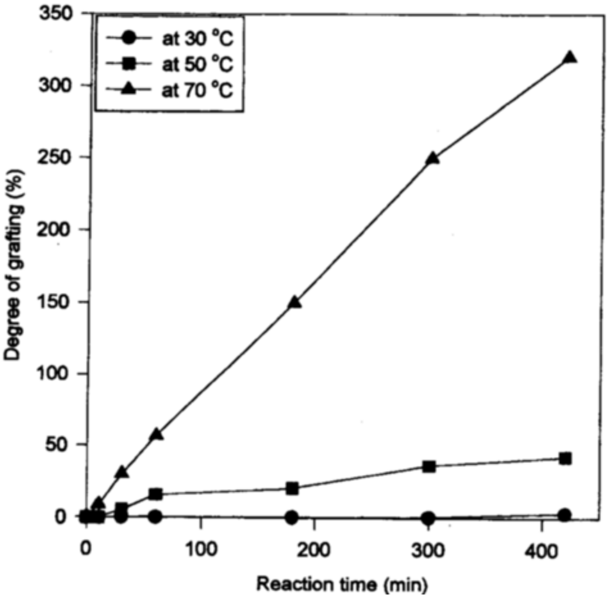


Fig. 3. Effects of reaction temperature and reaction time on the grafting onto PP fabrics.

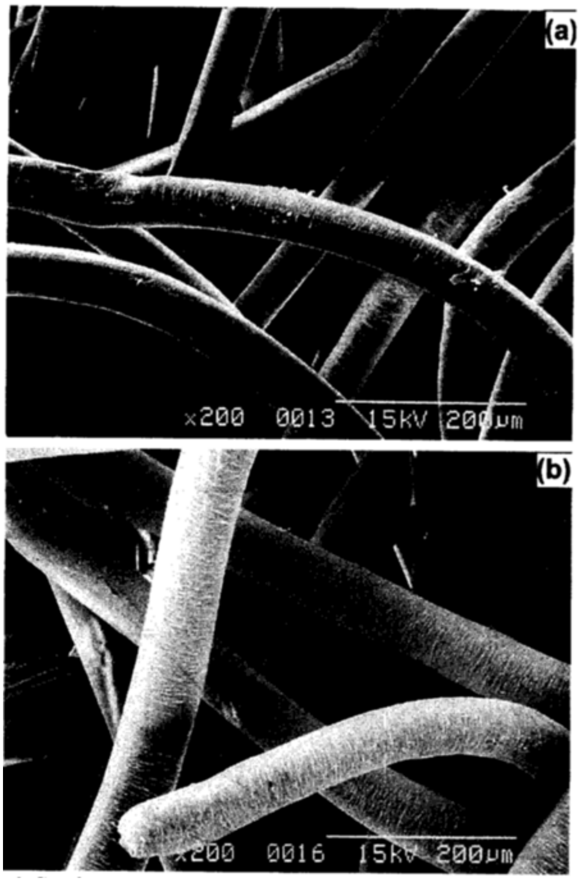


Fig. 4. Surface morphology of a base PP fabric and a 130 % GMA-grafted PP fabric.
(a) base PP fabric and (b) 130 % GMA-grafted PP fabric.

graft copolymerization. The greater decomposition of peroxide at higher temperatures probably accounted for the higher extent of grafting.

Fig. 4 shows the surface morphology of (a) Non-grafted PP fabrics and (b) 130 % GMA-grafted PP fabrics. The grafted PP fabrics led to the increase in the diameter and surface state of wool-line. This increase in diameter was due to the growth of graft chains inside the polymer matrix. Because the graft polymerization occurs mainly in the amorphous region of the matrix, the graft chain was thought to expand the amorphous region of the matrix. In other words, the grafting and the resultant expansion of the trunk polymer occur mainly at the mechanically weak part of the trunk polymer.

The TGA curves of ungrafted PP and grafted PP fabrics are shown in Fig. 5. The considerable change in the thermal behavior of PP fabric has occurred upon grafting. The initial decomposition temperature (IDT) and the final decomposition temperature (FDT) of the grafted PP were considerably lower than those of ungrafted PP. The decrease in IDT and FDT of PP after grafting shows evidence for grafting. Phosphoric acid (H_3PO_4) was reacted with 50 %-, 130 %-, and 250 %-grafted PP fabrics to make the PP fabric adsorbent modified with $-PO_3H$ group.

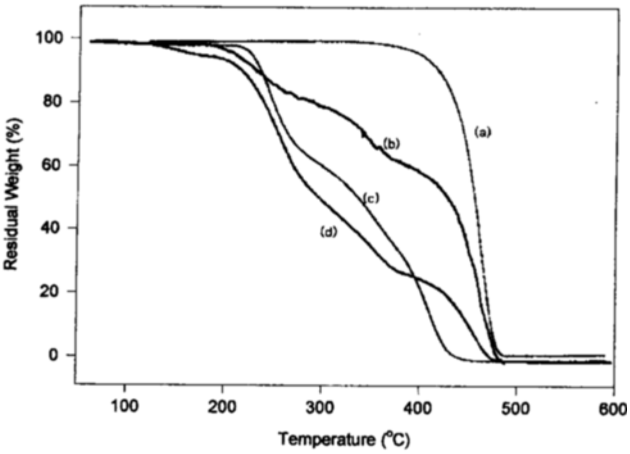


Fig. 5. TGA curves of (a) base PP fabric, (b) d.g.=50 %, (c) d.g.=130 %, and (d) d.g.=250 %.

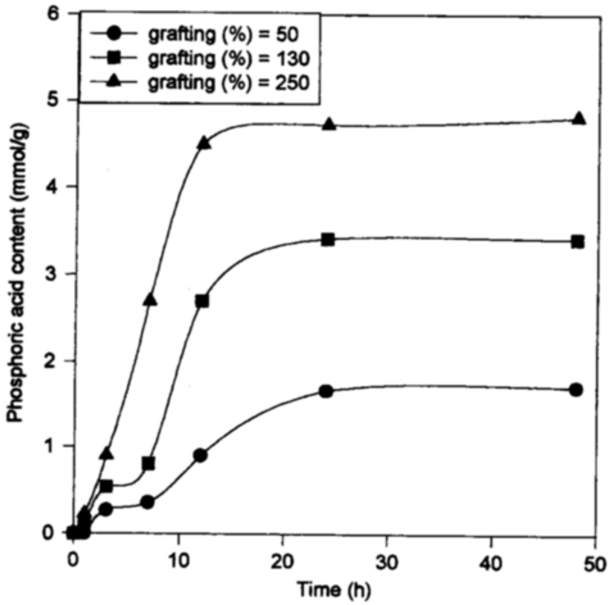


Fig. 6. Effect of reaction time on PP fabrics with 85 % H_3PO_4 aqueous solution at 80 °C.

The effects of reaction time on the content of phosphoric acid are shown in Fig. 6 when GMA-grafted fabric was placed in an 85 %-phosphoric acid aqueous solution at 80 °C for 1, 3, 7, 12, 24, and 48 h. The phosphoric acid content increased until 12 h, and then leveled off. The phosphoric acid content also increased with an increase in grafting yield.

The rate of adsorption of Pb^{2+}, Cu^{2+}, and Co^{2+} to PP fabric containing $-PO_3H$ (2.90 mmol/g) at room temperature is shown in Fig. 7. The Pb^{2+}, Cu^{2+}, and Co^{2+} increased with an increase in adsorption time to 24 h. The adsorption amount leveled off, and finally no further increase was observed. The adsorption amount of Pb^{2+} of the adsorbent containing 2.90 mmol/g of $-PO_3H$ for 24 h was *ca.* 79.0 g per kg. The adsorption amount of Co^{2+} for 24 h was *ca.* 75.5 g per kg. The adsorption amount of Cu^{2+} for 24 h was *ca.* 36.6 g per kg.

The amounts of Pb^{2+}, Cu^{2+} and Co^{2+} adsorbed by PP fabric containing various phosphoric acid contents are shown in Fig. 8. The amount of the Pb^{2+}, Cu^{2+} and Co^{2+} absorbed by the PP fabrics was determined by ICP. A higher phosphoric acid group

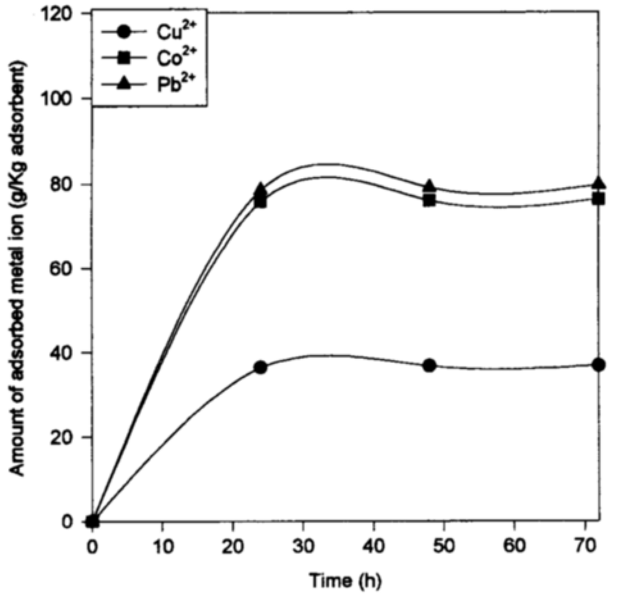


Fig. 7. The rate of adsorption of Pb^{2+}, Cu^{2+}, and Co^{2+} by PP fabric adsorbent (d.g.=250 %) with $-PO_3H$ group (2.90 mmol/g).

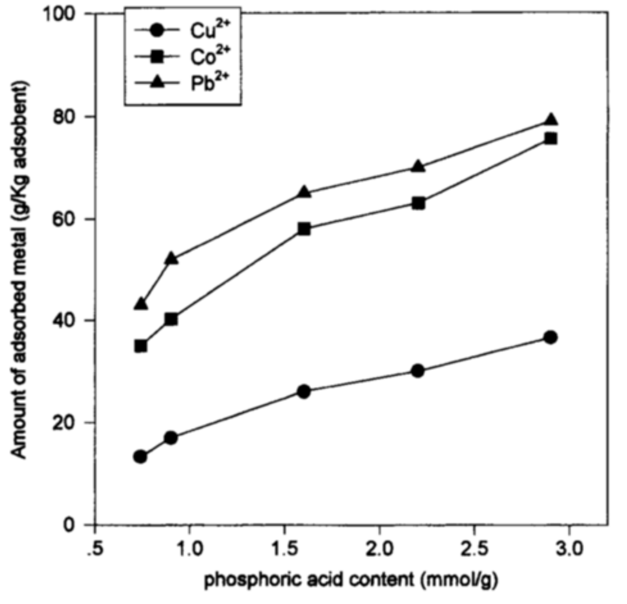


Fig. 8. Adsorption of metal ion by the PP fabric adsorbent (d.g.=250 %) with $-PO_3H$ group.

density resulted in higher amounts of adsorption. The order of adsorption of CEA containing $-PO_3H$ group was $Pb^{2+}>Co^{2+}>Cu^{2+}$.

2. Characterization of PE Hollow Fiber Adsorbent, and Its Adsorption Characterization to Pb^{2+}, Cu^{2+} and Co^{2+}

The relationship between the pore volume distribution and the grafting yield is shown in Fig. 9. The pore volume on a region ranging from a 1 to 10^{-1} μm pore diameter was found to be large. The pore volume decreased with increase in grafting yield. The pore volume of 2.6 L/kg of the PE hollow fiber was reduced to 1.75 L/kg with a 50 % grafting yield, and to 1.5 L/kg with an 80 % and 100 % grafting yield. The pore volume was approximately linearly proportional to the degree grafting of up to 80 %, but non-proportional beyond the grafting value.

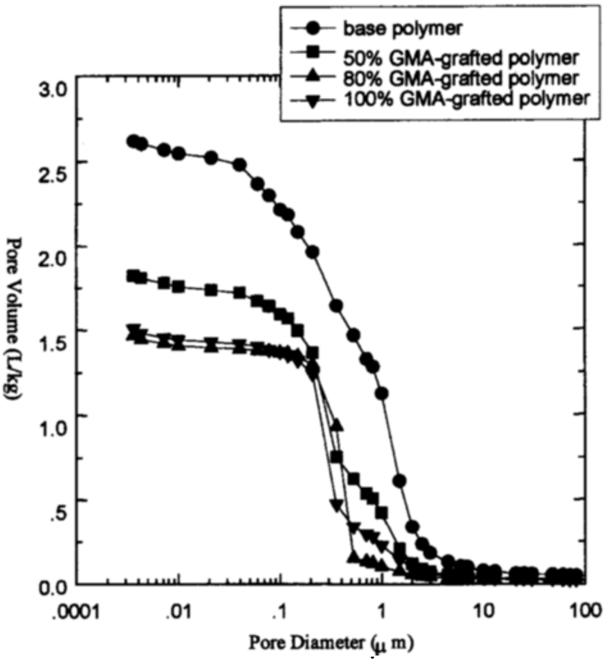


Fig. 9. Pore diameter distribution of polyethylene hollow fiber.

Fig. 10 shows the surface morphology of a base PE hollow fiber (a) and an 80 % GMA-grafted PE membrane (b). The pore size decreased with increase in grafting yield. This decrease was due to the growth of graft chains inside the pore.

The TGA curves of ungrafted PE hollow fiber and grafted GMA-grafted PE hollow fibers are shown in Fig. 11. The considerable change in the thermal behavior of the PE hollow fiber occurred upon grafting. The IDT and the FDT of GMA-grafted PE hollow fiber were considerably lower than those of ungrafted PE hollow fiber. The decrease in IDT and FDT of PE hollow fiber after grafting shows evidence for grafting. The properties of GMA-grafted PE hollow fiber and ungrafted PE hollow fiber are shown in Table 1. The conversion yield of the epoxy group on 80 % GMA-grafted PE hollow fiber was 1.21 mmol/g at 80 °C in 85 % H_3PO_4 aqueous solution for 24 h. The inner and outer diameter increased due to the grafting, whereas porosity, flux of pure water, and pore volume decreased. While this increase is due to the growth of the graft chains inside the polymer matrix, this decrease is due to the growth of the graft chains on the polymer matrix surface.

The breakthrough curves of Pb^{2+}, Cu^{2+}, and Co^{2+} for the ion-exchange hollow fiber modified $-PO_3H$ group are shown in Fig. 12. The inlet concentration of Pb^{2+}, Cu^{2+}, and Co^{2+} was 100 mg per liter (100 ppm), respectively. C/C^o remained zero until the permeation volume (PV) value reached 0.2, 0.06, 0.09 liter. After that point, C/C^o rose gradually with increase in PV. At $C/C^o=1$, the amount of Pb^{2+}, Cu^{2+}, and Co^{2+} adsorbed by the ion-exchange hollow fiber modified $-PO_3H$ group can be calculated from the area of PV times C, which is the upper portion above the breakthrough curves. The adsorption amounts of Pb^{2+}, Cu^{2+}, and Co^{2+} were 54.4, 21.1, and 32.1 g per kg, respectively. The order of

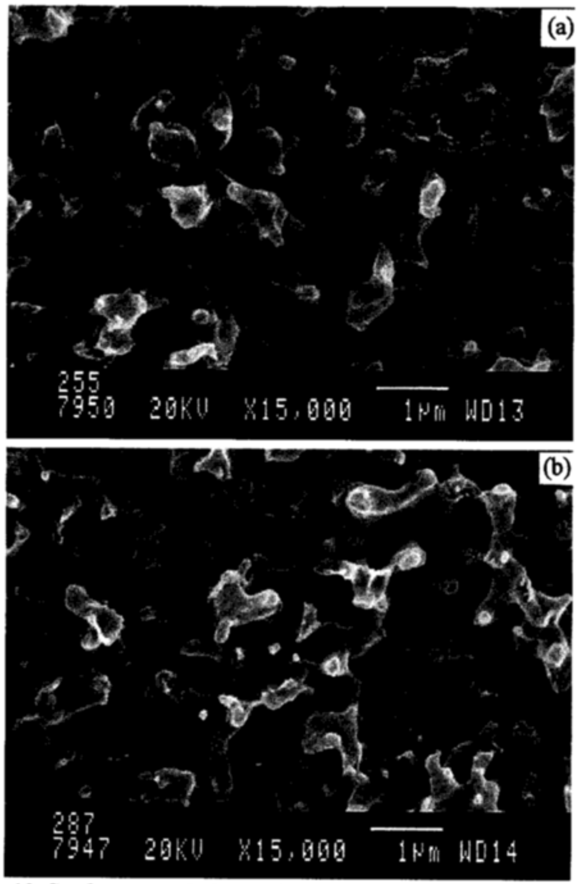


Fig. 10. Surface morphology of a base PE membrane and a 80 % GMA-grafted PE membrane.
(a) base PE membrane, (b) 80 % GMA-grafted PE membrane.

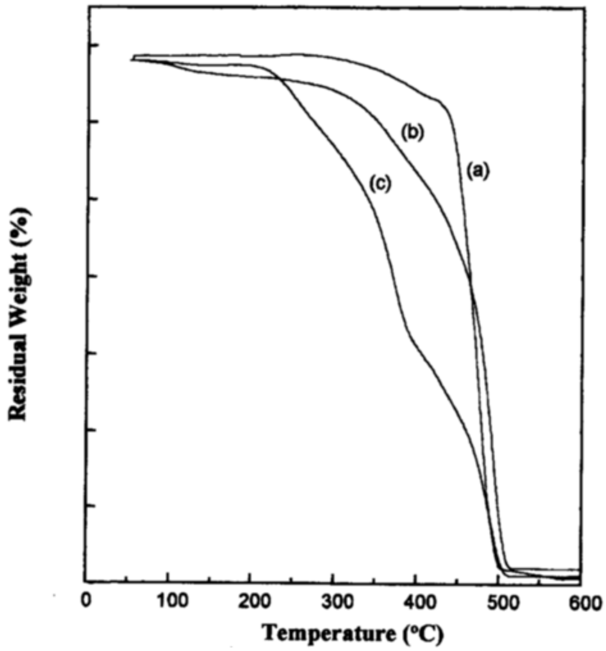


Fig. 11. TGA curves of (a) base PE hollow fiber, (b) d.g.=50 % and (c) d.g.=200 %.

adsorption of PE hollow fiber adsorbent was $Pb^{2+} > Co^{2+} > Cu^{2+}$.

Table 2 shows the properties of two ion-exchange hollow fibers. The IDT and FDT decreased due to the grafting. The adsorbed amounts of Pb^{2+}, Cu^{2+}, and Co^{2+} to PE hollow fiber matrix were 54.4, 21.1, and 32.1 g per kg, respectively. The

Table 1. Properties of ion-exchange hollow fiber adsorbent modified $-PO_3H$ group[a]

Properties	Ion-exchange adsorbent	PE hollow fiber
Degree of grafting (%)	80	-
Density of $-PO_3H$ (mmol/g)	1.21	-
Inner diameter (mm)	2.56	1.95
Outer diameter (mm)	4.80	3.01
Length (cm)	10	10
Porosity	60	71
Flux of pure water (m/h)[b]	0.34	3.12
Pore volume (cm/g)[c]	1.50	2.61

[a] 1.0×10^5 Pa.
[b] By a mercury intrusion method.

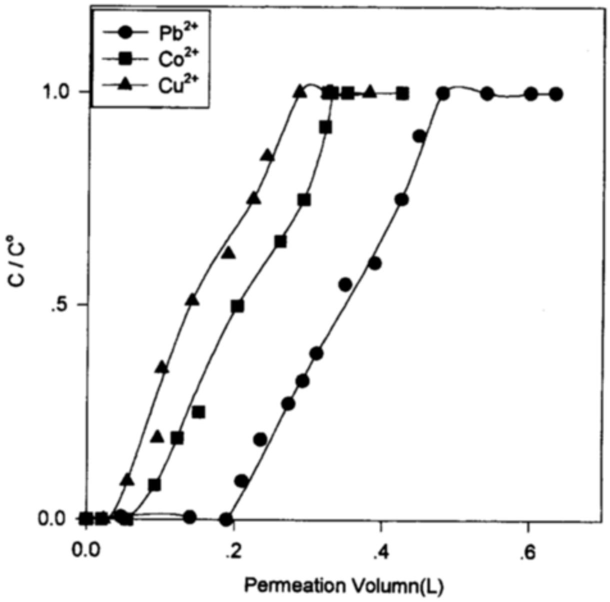


Fig. 12. Breakthough curves of Pb^{2+}, Cu^{2+}, and Co^{2+} ion to the PE hollow fiber adsorbent (d.g.=80 %) having $-PO_3H$ group of 1.21 mmol/g.

Table 2. Comparison of two ion-exchange adsorbents[a]

Properties	PP fabric adsorbent	PE hollow fiber adsorbent
Degree of grafting (%)	85	80
Initial decomposition temp. (°C)[b]	200(410)	290(450)
Final decomposition temp. (°C)[b]	480(485)	500(506)
Density of $-PO_3H$ (mmol/g)	1.21	1.21
Adsorption of metal ion (g/kg)	10	10
Pb^{2+}	58.6	54.4
Co^{2+}	42.3	32.1
Cu^{2+}	20.1	21.0

[a] Temperature obtained from trunk polymer are shown in parenthese.
[b] Not modified $-PO_3H$ group.

adsorbed amounts of Pb^{2+}, Cu^{2+}, and Co^{2+} by the PP fabric matrix were 58.6, 42.3, and 20.1 g per kg, respectively.

CONCLUSIONS

Attempts were made in this study to graft GMA onto PP fabric and PE hollow fiber and to introduce a phosphoric acid group onto GMA-grafted PP fabric and PE hollow fiber.

1. In the grafting of GMA onto PP fabrics, the degree of grafting (%) for GMA increased with an increase in reaction time, reaction temperature, and pre-irradiation dose. The maximum grafting yield was observed around 60 % GMA concentration.
2. Phosphoric acid was reacted with GMA-grafted PP fabric. In 50, 130, and 250 % GMA-grafted PP fabric, the content of phosphoric acid was 1.52, 3.40, and 4.50 mmol/g, respectively.
3. The adsorption of Pb^{2+} and Cu^{2+}, and Co^{2+} to the two ion-exchange adsorbents modified with $-PO_3H$ group was enhanced by increasing the phosphoric acid content. The order of adsorption to cation-exchange adsorbents is $Pb^{2+}>Co^{2+}>Cu^{2+}$.
4. In adsorption of Pb^{2+}, Cu^{2+} and Co^{2+} by the PE hollow fiber adsorbent, the amount of Pb^{2+} adsorbed to the PE hollow fiber adsorbent containing 1.21 mmol/g of $-PO_3H$ was *ca.* 54.4 g per kg. The adsorption amount of Cu^{2+} was *ca.* 21.1 g per kg. The adsorption amount of Co^{2+} was *ca.* 32.1 g per kg.
5. The order of adsorption by PE hollow fiber adsorbent is $Pb^{2+}>Cu^{2+}>Co^{2+}$.

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