Optimal Amidoximation Conditions of Acrylonitrile Grafted onto Polypropylene by Photoirradiation-Induced Graft Polymerization

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ABSTRACT: To prepare amidoxime (AO) adsorbents for uranium recovery from seawater, the optimum conditions for graft polymerization and amidoximation of acrylonitrile (AN) group and alkaline treatment of the AO group have been investigated in terms of the uranium adsorption capacity. AN has been grafted onto polypropylene (PP) fabric by photoirradiation-induced graft polymerization with benzophenone as the photoinitiator. A concentration of AN $\leq 1.0M$, a photoirradiation time of 2 h, and a reaction temperature of 60°C proved to be optimal for the grafting of AN onto PP. The grafted AN groups were effectively converted into AO groups upon reaction with $\geq 5.0\%$ (w/v) hydroxylamine solution at pH 7.0−9.0 for ≥ 16 h at 60−80°C. Although widely used for this purpose, we have shown that methanol is not an essential solvent for the amidoximation reaction. Conditioning of the AO group with KOH solution (alkaline treatment) proved to be effective for enhancing the uranium adsorption capacity of amidoximated PP-g-AN-AO fabric, which increased logarithmically with the conditioning time. The AO group density in the PP-g-AN-AO fabric increased linearly with the degree of AN grafting, whereas the uranium adsorption capacity of PP-g-AN-AO fabric conditioned with KOH reached a maximum at a degree of AN grafting of approximately 60%. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 125: 776–785, 2012

Key words: photoinduced grafting; acrylonitrile; amidoximation; alkaline treatment; uranyl ion adsorption

INTRODUCTION

Various polymeric adsorbents with specific functionalities have been developed for the removal or selective recovery of target metal ions from aqueous solutions. Such polymeric adsorbents have been synthesized either by polymerizing monomers possessing functional groups capable of interacting with the target metal ions or by converting groups on existing polymers or copolymers into the desired functional groups with suitable reactants.[1–5] Many kinds of functional groups, such as carboxyl, phosphoric acid, sulfonic acid, thioamide, imidazoline, amine, amidoxime (AO), etc., have been studied for their potential applications in separating metal ions from aqueous solutions.[6−11] Among them, the AO functional group has attracted widespread attention during the last three decades because of its high potential for selectively recovering uranium from seawater. Extensive studies on adsorbents containing the AO functional group have been carried out to investigate the preparation and properties of new copolymers with balanced hydrophilic and AO group contributions for the uptake of uranyl ions from aqueous solutions.[12−16]

The standard process for preparing adsorbents containing AO groups involves three steps: (i) graft polymerization of acrylonitrile (AN) onto the substrate polymer (AN grafting), (ii) chemical conversion of the nitrile (CN) group into an AO group (amidoximation), and (iii) conditioning of the AO group with alkaline solution (alkaline treatment).[17,18] Systematic optimization of this preparation process has proved effective for improving the adsorption characteristics of uranium from seawater, such as adsorption rate, adsorption capacity, and durability. Despite the extensive studies on the preparation of AO-containing adsorbents, information on the optimum reaction conditions for the amidoximation and alkaline treatment is still limited because few researchers have addressed them systematically. In general, AO groups are introduced by reacting an AN-grafted polymer with 3% (v/v) hydroxylamine in 50/50 (v/v) methanol/water (pH 7) for 2 h at 80°C. The alkaline treatment of the amidoximated graft polymer is generally conducted with 2.5 wt % KOH solution for 1−2 h at 80°C. However, different

reaction conditions have been applied to the amidoximation of AN-grafted polymers with varying degrees of success. For example, Şahiner et al.[19] successfully converted 99% of the CN groups of polyacrylonitrile into AO groups by reacting with 0.05M hydroxylamine for 20 h at 50°C. Pantchev et al.[20] carried out the amidoximation of AN-grafted nylon-6,6 discs by treating them with 52% (w/v) hydroxylamine in water for 8 h at 55°C. More recently, Liu et al.[21] converted the CN groups in AN/methyl acrylate copolymer beads into AO groups by reaction with approximately 60 wt % hydroxylamine solution (pH 8) for 20 h at 70°C.

Okamoto et al.[17] investigated the effect of temperature on the amidoximation of AN-grafted polypropylene (PP) and polyethylene fibers. They reported that the conversion was less than 5% at 40°C even after 10 h, but exceeded 60% after 6 h when the temperature was raised to the boiling point of hydroxylamine solution (80°C). However, Das et al.[22] reported that 75−80% of the CN groups in AN-grafted PP fibrous sheet could be converted into AO groups by treatment with 3% hydroxylamine solution (methanol/water, 1:1) at 60°C for 8 h.[22] Recently, Saeed et al.[23] investigated the effects of the concentration of hydroxylamine and reaction time on the amidoximation of polyacrylonitrile nanofibers, and concluded that the conversion of the CN groups in polyacrylonitrile increased with increasing concentration of hydroxylamine and extending the reaction time, due to enhancement of the molecular diffusion of hydroxylamine from the solution into the nanofibers.

The objective of this study has been to find the optimum reaction conditions for the amidoximation and alkaline treatment of AN-grafted PP nonwoven fabric prepared by conventional photoirradiation-induced graft polymerization. The effects of several parameters, such as the degree of grafting, the concentrations of hydroxylamine and solvent, the pH of the hydroxylamine solution, and the reaction time and temperature, on the amidoximation of AN-grafted PP nonwoven fabric and the uranium adsorption capacity of the product have been investigated to determine the optimum reaction conditions for amidoximation. Experiments have also been conducted to confirm the effect of alkaline treatment of the amidoximated graft fabric with KOH solution on the uranium adsorption capacity.

EXPERIMENTAL

Reagents

Nonwoven PP fabric (180 g/m^2) used as the substrate polymer for grafting was obtained from the Samsung Non-woven Fabric, Seoul, Korea. The monomer used was AN (Sigma-Aldrich, Milwaukee, WI), the photoinitiator was benzophenone (BP; Yakuri Pure Chemical Co., Osaka, Japan), and the solvents used were methanol and deionized water. Hydroxylamine hydrochloride (NH$_2$OH·HCl; Daejung Chemical Co., Seoul, Korea) was used as the amidoximation reagent for converting CN functional groups of the AN grafted onto PP nonwoven fabric into AO functional groups. All reagents were of the highest grade available and were used as received.

Seawater sampled at the seashore of Muan bay on the southwestern coast of Korea was used after filtering through a 0.45-μm pore size membrane filter. The seawater used for the adsorption experiments was prepared by dissolving uranyl nitrate hexahydrate (UO$_2$(NO$_3$)$_2$·6H$_2$O; Sigma-Aldrich) in the filtered seawater to give a uranium concentration of 1.0 mg/L.

Graft polymerization of AN onto PP

The PP nonwoven fabric was cut into strips (1 cm wide and 10 cm long), washed with a neutral detergent solution, and then air-dried at 60°C. The monomer solution was prepared with 70/30 (v/v) water/methanol, and contained 0.5−1.5M AN and 0.2% (w/v) BP. One piece of PP fabric was placed in a Pyrex glass tube containing 20 mL of the monomer solution, the solution was purged with nitrogen to eliminate oxygen, and then the tube was sealed. The tube was exposed to ultraviolet light for 1−5 h at 60°C. The light source was a 400 W high-pressure mercury lamp (Miya Electric Co., Gwangju, Korea) and the glass tubes were simultaneously rotated and revolved around the light source at a distance of 10 cm. After the grafting reaction, the PP fabric was removed from the glass tube, washed three times with hot water, extracted with methanol for 3 h in a Soxhlet apparatus to remove unreacted monomer and homopolymer, and finally air-dried at 60°C to constant weight. The degree of grafting was calculated from the weight gain:

$$\text{Degree of grafting } (\%) = \frac{(W_1 - W_0)}{W_0} \times 100 \quad (1)$$

where W_0 and W_1 are the weights of the substrate and the grafted fabric, respectively.

Amidoximation of grafted AN

AN-grafted PP (PP-g-AN) nonwoven fabric was immersed in hydroxylamine solution to convert the CN groups of the grafted AN into AO groups. The hydroxylamine solution was prepared with 0−75% (v/v) methanol solution, contained 3–10% (w/v) NH$_2$OH·HCl, and its pH was adjusted between 3.6
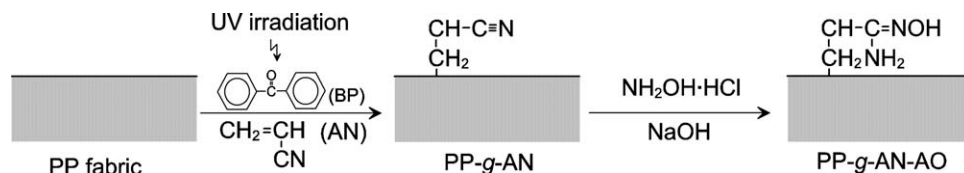
Figure 1 Preparation and chemical structure of PP-*g*-AN-AO.

and 12.0 using NaOH solution. The amidoximation reaction was conducted for 3–36 h at 20–100°C with periodic stirring. After the reaction, the amidoximated PP-*g*-AN (PP-*g*-AN-AO) nonwoven fabrics were repeatedly washed with deionized water to remove the residual and unreacted solution, and then air-dried at 60°C to constant weight. The conversion ratio of AN to AO and the AO group density were calculated from the weight gain and the molar ratio between AN and AO as follows:

$$\text{Conversion of AN to AO (\%)} = \frac{(W_2 - W_1)/33}{(W_1 - W_0)/53} \times 100 \tag{2}$$

$$\text{AO group density (mmol/g)} = \frac{(W_2 - W_1)/33}{W_2} \times 1000 \tag{3}$$

where W_2 is the weight of the PP-*g*-AO fabric after amidoximation, and the values 33 and 53 are the molecular masses of hydroxylamine and AN monomer, respectively.

The PP-*g*-AN-AO fabrics were conditioned by treating them with 2.5% (w/v) KOH solution at 80°C for 1–24 h and then washing with deionized water until the washings were neutral. The synthetic route and the chemical structure of PP-*g*-AN-AO nonwoven fabric are shown in Figure 1.

Characterization of graft and amidoximated polymer

The chemical structures of the substrate PP, PP-*g*-AN, PP-*g*-AN-AO, and PP-*g*-AN-AO treated with KOH (PP-*g*-AN-AO-KOH) were analyzed with an infrared spectrophotometer (Shimadzu IR-435, Kyoto, Japan). The surface morphologies were observed with a field-emission scanning electron microscope (SEM; Hitachi S-4800, Tokyo, Japan). The potentiometric titration method was used to evaluate the surface charges of PP-*g*-AN, PP-*g*-AN-AO, and PP-*g*-AN-AO-KOH as described previously.[24] The fabric was cut into $\sim 5 \times 5$ mm^2 pieces and mixed with 0.01M NaNO$_3$ to obtain a 2-g/L suspension, which was stirred with a magnetic follower and kept at 20°C. The mixture was titrated by the addition of 0.1M HNO$_3$ or 0.1M NaOH with a micropipette. The pH range 2.0 to 12.0 was covered using a

bench-top pH meter (Thermo Scientific Orion 3-Star, Waltham, MA). The surface charge density σ (C/cm^2) was calculated as a function of pH from the difference between the total added acid or base and the equilibrium concentration of H$^+$ and OH$^-$ for a given quantity W (g/L) of fabric using the following equation:

$$\sigma = \frac{F(C_A - C_B + [\text{OH}^-] - [\text{H}^+])}{WA} \tag{4}$$

where F is Faraday's constant (96,490 C/mol); C_A and C_B are the concentrations (mol/L) of acid and base, respectively, after each addition during the titration; [H$^+$] and [OH$^-$] are the equilibrium concentrations of H$^+$ and OH$^-$, respectively; and A is the surface area of the fabric used (cm^2/g).

Adsorption experiments were carried out under batch conditions, whereby 0.4 g of each fabric was added to a 1-L flask containing 500 mL of seawater spiked with uranium (1 mg/L). The flask was placed in an incubator shaker (25°C) and then continuously shaken at 120 rpm for 7 days. After the adsorption reaction, the fabric was removed from the flask, washed briefly with deionized water, and then centrifuged at 2000 rpm for 5 min to remove entrained seawater. The centrifuged fabric was immersed in 20 mL of 1M HCl and shaken at 25°C for 2 h to release the adsorbed uranium. The uranium desorbed into the HCl solution was determined by inductively coupled plasma analysis (ICP-AES, Spectro Analytical Instruments, Kleve, Germany). The sorption capacity, q (mg/g), was calculated using the following equation:
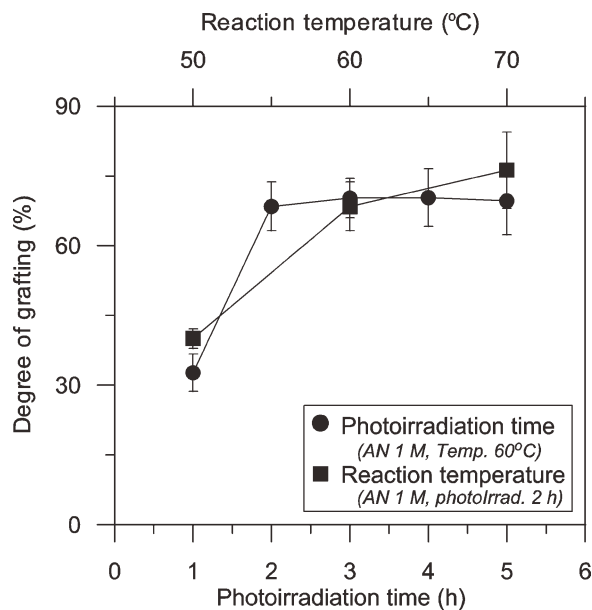
$$q = \frac{CV}{W} \tag{5}$$

where C is the concentration of uranium in the HCl solution (mg/L), V is the volume of HCl solution used (L), and W is the dry weight of sorbent used (g).

RESULT AND DISCUSSION

Preparation of PP-*g*-AN

As described in the Experimental Section, PP-*g*-AN nonwoven fabric was prepared by a conventional

Figure 2 Effect of photoirradiation time and reaction temperature on the degree of AN grafting.

photoirradiation-induced graft polymerization technique, which is an excellent and well-established technology for introducing ion-exchange and chelation functions into a variety of shapes of conventional polymers.[25–27]

To identify the optimum conditions for photografting of AN onto PP nonwoven fabric, the effects of photoirradiation time, reaction temperature, and monomer concentration on graft polymerization were investigated. Figure 2 shows the degree of AN grafting onto PP obtained with $1.0M$ AN, 0.2% (w/v) BP, and 30% (v/v) methanol in deionized water and photoirradiation times in the range 1–5 h at different reaction temperatures of $50-70°C$. The degree of grafting increased greatly with the photoirradiation time up to 2 h. However, it almost leveled off after 2 h, probably due to a large amount of homopolymer formation in the residual monomer solution, which would decrease the monomer available for graft polymerization. The degree of grafting increased with the reaction temperature. However, the relative rate of increase in the degree of grafting tended to decrease, whereas the standard deviation ($n = 3$) increased, with increasing reaction temperature. Figure 3 shows the degree of grafting for various concentrations of AN. All experiments were performed with a monomer solution containing $0.5-1.5M$ AN, 0.2% (w/v) BP, and 30% (v/v) methanol in deionized water, with a photoirradiation time of 2 h at 60°C. The degree of grafting increased with increasing concentration of AN. However, the increase in standard deviation ($n = 3$) for the degree of grafting with increasing AN concentration indicates that the reproducibility of the graft polymeriza-

tion decreased with increasing AN concentration, especially when the latter exceeded $1.0M$. Thus, although increasing the AN concentration is a facile method for enhancing the degree of grafting, it is difficult to increase the degree of grafting to >80% and to control the reproducibility for high degrees of grafting. Figure 3 also shows the difference in degree of grafting between washing with hot water and subsequent Soxhlet extraction with methanol. This difference tended to increase slightly with the AN concentration but was not significant even at $1.5M$ AN. This indicates that unreacted monomer and homopolymer on the grafted fabric could be almost completely removed by a simple washing with hot water alone.

From these observations, a concentration of AN $\leq 1.0M$, a photoirradiation time of 2 h, and a reaction temperature of 60°C were selected as the optimum conditions for the preparation of PP-g-AN nonwoven fabric using a photoinduced graft polymerization. The PP-g-AN nonwoven fabrics synthesized under these conditions were used as substrates for further studies on the preparation of adsorbents containing AO groups.

Preparation and characterization of PP-g-AN-AO

PP-g-AN-AO fabric was prepared according to a conventional method. The PP-g-AN fabrics were reacted with hydroxylamine to convert AN to AO groups, and subsequently conditioned by treating them with KOH solution. In this way, we could prepare PP-g-AN-AO fabrics with $60 \pm 10\%$ AN-grafted chains, of which $80 \pm 5\%$ were converted
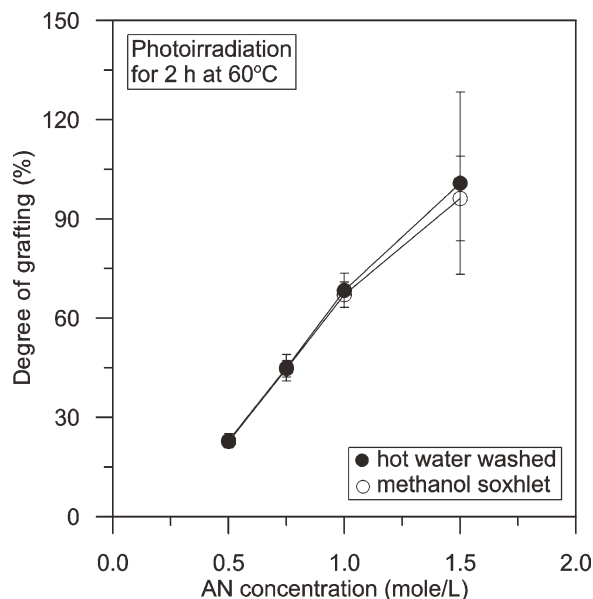
Figure 3 Effect of the concentration of AN on the degree of AN grafting.
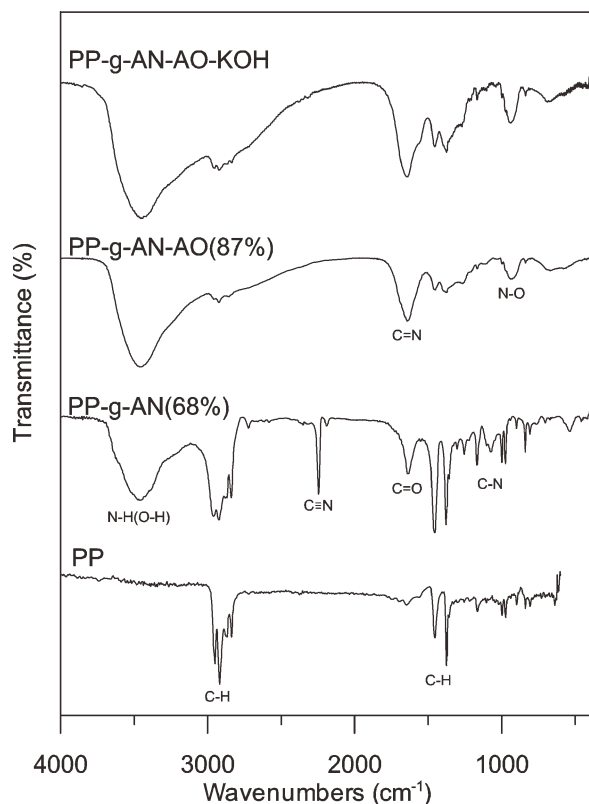
Figure 4 FTIR spectra of PP substrate, PP-*g*-AN, PP-*g*-AN-AO, and PP-*g*-AN-AO-KOH.

into AO groups, and their alkaline-treated form, PP-*g*-AN-AO-KOH. Thus, the fabrics prepared were used in all experimental studies relating to characterization.

The FTIR spectra obtained from substrate PP, grafted PP-*g*-AN, amidoximated PP-*g*-AN-AO, and alkaline-treated PP-*g*-AN-AO-KOH are presented in Figure 4. Compared with the spectrum of the substrate PP, a new absorption peak was observed in the spectrum of PP-*g*-AN at 2245 cm^{-1}, corresponding to the C≡N groups of the AN grafted onto PP, along with several different unexpected absorption peaks at 1080–1305 cm^{-1}, 1640 cm^{-1}, and 3480 cm^{-1} relating to C—N, N—H (or C=O), and O—H (or N—H), respectively, of amines and amides. These absorption peaks clearly indicate the formation of amide or amine groups during the photografting of AN onto PP, which may be due to partial hydrolysis of the grafted AN and subsequent amidoximation, although further studies are required to confirm this. After the amidoximation of PP-*g*-AN, the C≡N band at 2245 cm^{-1} was seen to decrease with depletion of the CN groups of AN-grafted chains, while a C=N stretching vibration at 1650 cm^{-1} and an N—O stretching vibration at 940 cm^{-1} appeared, indicating the formation of AO groups. No new peaks were observed in the spectrum of the alkaline-treated form, PP-*g*-AN-AO-KOH.

Figure 5 shows SEM images of (a) the substrate PP, (b) PP-*g*-AN, and (c) PP-*g*-AN-AO. The PP fiber swelled as a result of the grafting of AN and subsequent amidoximation of the grafted AN with hydroxylamine, and showed a clear tendency of the surface becoming rougher and more heterogeneous with the grafting and amidoximation. The average diameters of the substrate PP fibers, 70% AN-grafted fibers, and the amidoximated fibers (82%) were determined to be 27.0 ± 2.2, 40.8 ± 6.5, and 41.9 ± 6.8 μm, respectively.

The effects of AN grafting, amidoximation, and alkaline treatment on the surface charge density of the PP fiber were also investigated. As shown in Figure 6, the surface charge density of PP-*g*-AN was nearly constant over the pH range 4–8, whereas the surface charge densities of PP-*g*-AN-AO and PP-*g*-AN-AO-KOH became more positive with decreasing pH. These results indicate that amidoximation and subsequent alkaline treatment led to a positive potential on the surface of the PP fiber. The values of pH_{pzc} determined from the point of intersection zero charge (σ_o) with the pH curves were 5.5, 6.0, and 8.6 for PP-*g*-AN, PP-*g*-AN-AO, and PP-*g*-AN-AO-KOH, respectively.

To evaluate the effects of amidoximation and alkaline treatment on the uranium adsorption capacity of the PP-*g*-AN fabric, batch adsorption tests were carried out using seawater spiked with uranium (1 mg/L). As shown in Table I, the alkaline-treated PP-*g*-AN-AO-KOH fabric exhibited a much higher uranium adsorption capacity than the PP-*g*-AN fabric and even than the untreated PP-*g*-AN-AO fabric. The uranium uptake on the PP-*g*-AN-AO-KOH fabric was found to be approximately 10 times higher than that obtained with the untreated PP-*g*-AN-AO fabric. Similar observations have been reported for graft polymers containing AO or AO-*co*-hydrophilic monomer.[28,29] This is assumed to be due to a structural change of the AO polymers such that the space between the polymer chains is increased by the alkaline treatment at high temperature, which results in enhanced sorption of water.[28] The results shown in Table I indicate that the alkaline treatment of the AO groups is essential for enhancing the AO functionality in the recovery of uranium from seawater.

Optimization of the amidoximation conditions

In the amidoximation reaction for converting AN to AO, methanol has usually been used as a solvent in the preparation of hydroxylamine solution,[30] with only a few exceptions.[20,23] However, the exact role of methanol in the amidoximation of AN groups has not been confirmed. Thus, the effect of the methanol concentration in the hydroxylamine solution on the conversion of AN to AO was first investigated using

(a) PP fiber

(b) PP-*g*-AN fiber

(c) PP-*g*-AN-AO fiber
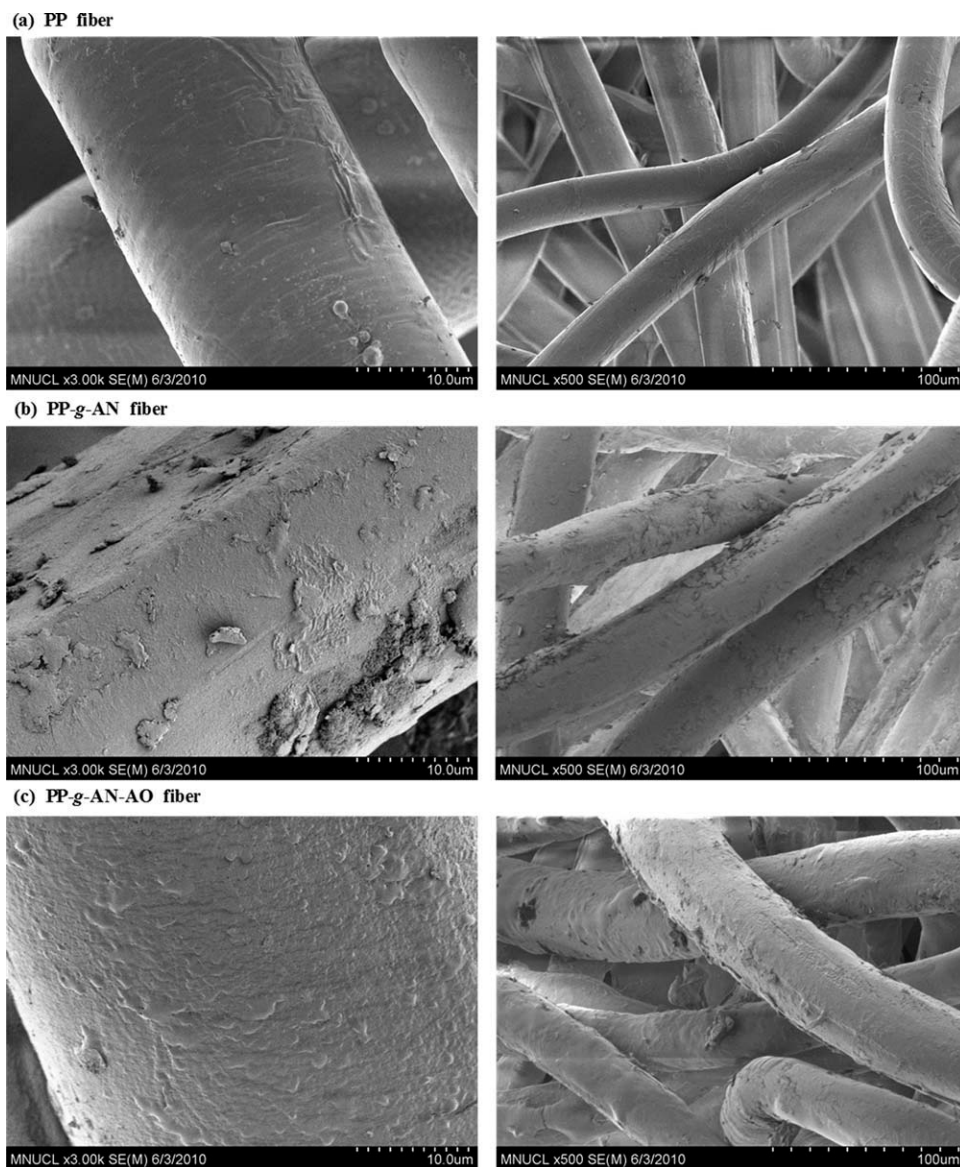
Figure 5 SEM images of PP substrate (a), PP-*g*-AN (b), and PP-*g*-AN-AO (c).

a hydroxylamine solution containing 10% (w/v) $NH_2OH \cdot HCl$ and 0–75% (v/v) methanol in deionized water, adjusted to pH 7.0 using NaOH solution. The amidoximation reaction was conducted for 24 h at 80°C with periodic stirring. Figure 7 shows the conversion ratio of AN to AO and the uranium uptakes in the resulting amidoximated graft polymer, PP-*g*-AN-AO, for various concentrations of methanol. The conversion ratio of AN to AO and the AO group density were nearly constant for different concentrations of methanol, clearly indicating that the amount of methanol in the hydroxylamine solution did not have a significant effect on these parameters. On the other hand, the uranium uptakes in the PP-*g*-AN-AO fabrics, which were conditioned with 2.5% (w/v) KOH solution at 80°C for 24 h

before using them for adsorption experiments, tended to increase slightly with the methanol concentration and were maximized on average at 20% (v/v) methanol. However, the extents of increase were limited almost to within the range of standard deviation obtained for each condition, as shown in Figure 7. This also supports the view that methanol is not an essential solvent for the amidoximation reaction. Therefore, hydroxylamine solutions prepared by using only deionized water were used for further experiments.

The conversion ratio of AN to AO for different concentrations of hydroxylamine and the AO group density of the resulting PP-*g*-AN-AO are shown in Figure 8. All of these experiments were carried out for 24 h at 80°C with 3–10% (w/v) $NH_2OH \cdot HCl$ in
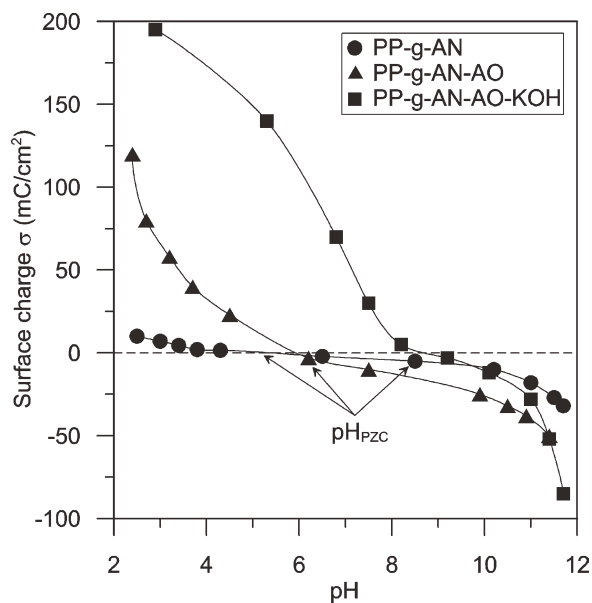
Figure 6 Surface charge density of PP-g-AN, PP-g-AN-AO, and PP-g-AN-AO-KOH as a function of pH.

deionized water (pH 7.0). As shown in Figure 8, the conversion ratio of AN to AO increased from 67.3 ± 1.5 to 83.5 ± 4.4% as the concentration of hydroxylamine was increased from 3 to 5% (w/v) and then almost leveled off.

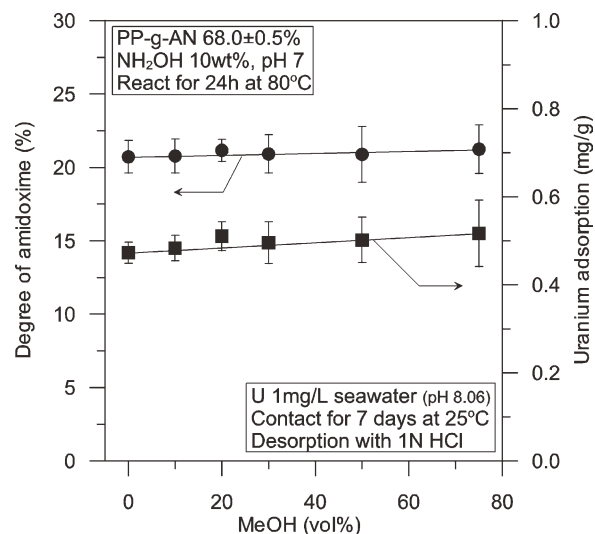The effects of amidoximation temperature and time on the conversion of AN to AO were investigated to determine the optimal reaction conditions for amidoximation. All of these experiments were performed with an excess of hydroxylamine solution containing 7.5% (w/v) $NH_2OH \cdot HCl$ in deionized water to ensure maximum possible conversion of AN to AO.

Figure 9 shows the conversion ratio of AN to AO and the AO group density at different amidoximation temperatures. The conversion of AN to AO increased rapidly from 8.6 ± 0.4% to 82.8 ± 0.6% on increasing the amidoximation temperature from 40 to 60°C, reached its maximum of 89.1 ± 0.7% at 80°C, corresponding to the boiling point of hydroxylamine solution, and then tended to slightly decrease with a further increase in temperature. Sim-

TABLE I
Uranium Adsorption Capacities of PP-g-AN,
PP-g-AN-AO, and PP-g-AN-AO-KOH Fabrics

| Reaction sequence	U adsorption (mg/g)[a]
PP-g-AN(52.2%)	0.015 ± 0.003
PP-g-AN(52.7%)-AO(88.1%)	0.053 ± 0.007
PP-g-AN(55.0%)-AO(89.6%) treated with KOH	0.466 ± 0.040

[a]Contacted with seawater containing U = 1.0 mg/L (pH 8.06) for 7 days at 25°C, desorption of U adsorbed with 1 N HCl.

Figure 7 Conversion ratio of AN to AO and uranium uptake in amidoximated fabric as a function of the concentration of MeOH in NH_2OH solution.

ilar observations were reported by Okamoto et al.[17] who investigated the effect of temperature on the amidoximation of AN-grafted fibers.

Figure 10 shows the conversion ratios of AN to AO and the AO group densities of PP-g-AN-AO samples obtained with various degrees of AN grafting at 80°C and amidoximation times in the range 3–36 h. Regardless of the degree of grafting, the conversion ratio of AN to AO increased with the amidoximation time up to 16 h and then leveled off thereafter, as shown in Figure 10(a). A maximum of approximately 90% conversion ratio was achieved for all degrees of grafting tested. As shown in Figure 10(b), similar time-dependent behavior was also
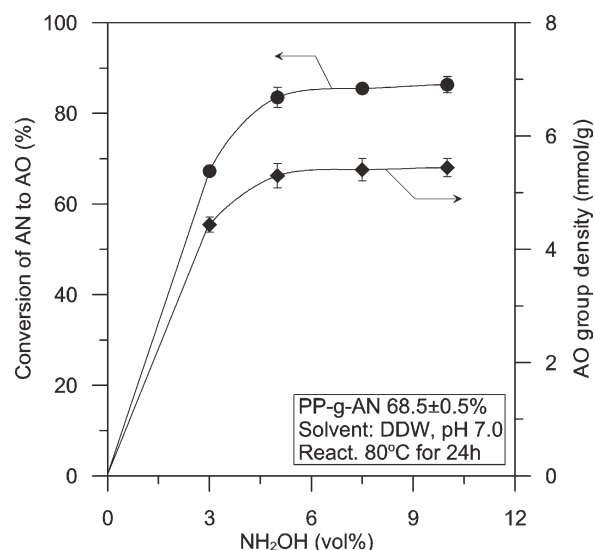
Figure 8 Effect of the concentration of NH_2OH on the conversion ratio of AN to AO and the AN group density in the amidoximated fabric.
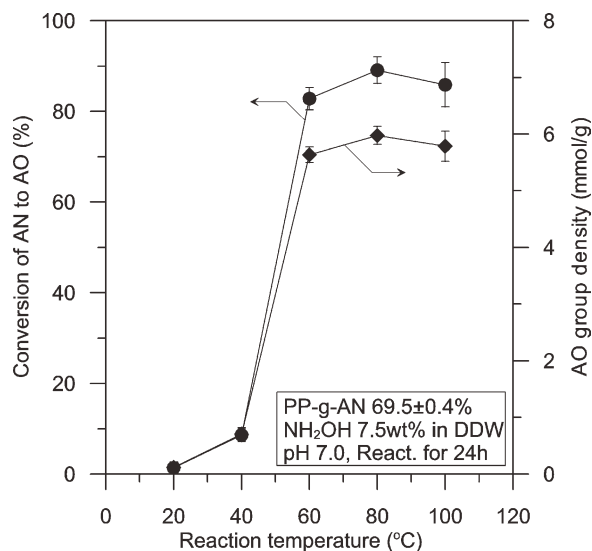
Figure 9 Effect of amidoximation temperature on the conversion ratio of AN to AO and the AN group density in the amidoximated fabric.

observed for the AO group density. However, in contrast to the conversion ratio, the AO group density increased with the degree of grafting. This is an expected result because the number of AN groups available for amidoximation is directly proportional to the degree of grafting. The linearity of a graph of AO group density versus degree of grafting is shown in Figure 11. In contrast, the uranium adsorption capacities of PP-g-AN-AO fabrics conditioned with 2.5% KOH at 80°C for 24 h increased with the degree of grafting up to approximately 60% and then decreased with any further increase, as shown

in Figure 11. The decreasing trend for high degrees of grafting may be due to the fact that fibers gradually increase in thickness with increasing degree of grafting, thereby relatively decreasing the effective surface area bearing the adsorptive functional groups on PP-g-AN-AO fabrics, so that uranyl ions are able to diffuse lesser into the interior. From this result, the optimal degree of grafting in terms of uranium adsorption capacity was found to be 60 ± 5%.

The pH of the hydroxylamine solution is an important determinant in the amidoximation reaction for the conversion of AN to AO. To identify the effects of the pH of the hydroxylamine solution on the conversion of AN to AO and the uranium adsorption capacity of the resulting PP-g-AN-AO fabric, amidoximation experiments were carried out for 24 h at 80°C with 7.5% (w/v) hydroxylamine solutions adjusted to pH 3.6−12.0 by adding NaOH solution. Figure 12(a) shows the conversion ratio of AN to AO and the AO group density in the resulting product, PP-g-AN-AO fabric obtained at different pH levels of the hydroxylamine solution. The conversion of AN to AO increased with increasing pH of the hydroxylamine solution up to 9.0 and tended to decrease with a further increase. A maximum of 95% conversion of AN groups to AO groups was achieved with a hydroxylamine solution at pH 9.0, which was approximately 5% higher than that at pH 7.0, the pH generally regarded as optimal in most literature reports. The calculated AO group densities in PP-g-AN-AO fabrics (64.3 ± 1.9% AN grafting) amidoximated with hydroxylamine solutions at pH 7.0 and 9.0 were 5.43 ± 0.13 and 5.67 ± 0.07 mmol/g, respectively. On the other hand, the
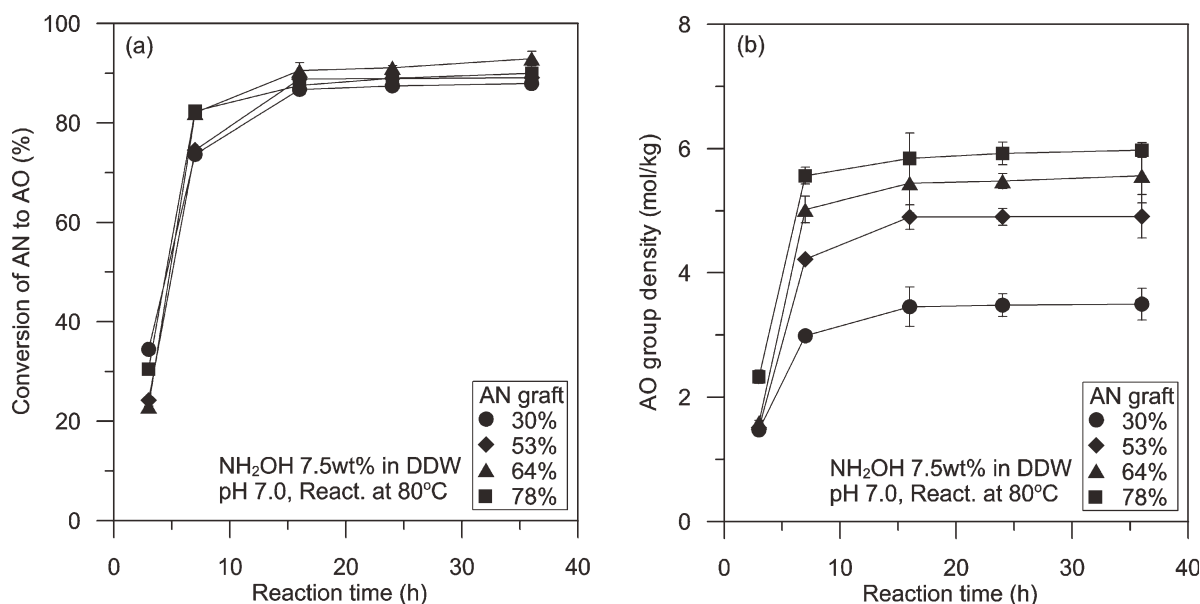
Figure 10 Conversion ratio of AN to AO (a) and AO group density (b) in the amidoximated fabric with various degrees of AN grafting as a function of photoirradiation time.
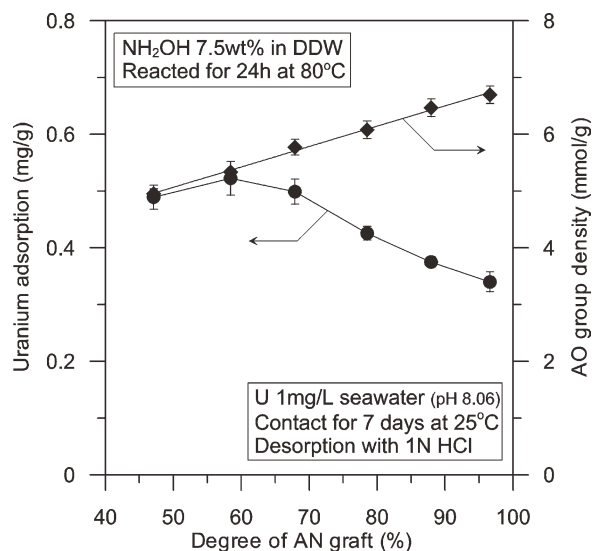
Figure 11 AO group density and uranium adsorption capacity of amidoximated fabric as a function of the degree of AN grafting. The amidoximated fabrics were conditioned with KOH before adsorption experiments.

uranium uptake on the PP-g-AN-AO fabric was found to increase consistently with increasing pH of the hydroxylamine solution, as shown in Figure 12(b). Moreover, it was also found that the uranium uptake continued to increase significantly on increasing the pH of the hydroxylamine solution up to 12.0, even though the AO group density decreased. A possible explanation for this result is that a structural change of the graft chains took place during the amidoximation reaction at higher pH of the hydroxylamine solution, similar to the effect of alkaline treatment.[28] Although it is the case that performing the amidoximation at high pH of the hydroxylamine

solution led to a greatly enhanced uranium uptake ability of the resulting products, it should be noted that their uranium uptakes were still be much lower than that observed for PP-g-AN-AO prepared by a two-step process involving amidoximation and subsequent alkaline treatment. Considering the AO conversion and uranium recovery from seawater, a recommendable pH for the hydroxylamine solution would seem to be in the range of 7–9.

As described above, conditioning of the AO group with alkaline solution (alkaline treatment) is also an important factor for improving the adsorption capacity of amidoximated graft polymers for uranium. Figure 13 shows the adsorption of uranium on PP-g-AN-AO-KOH fabrics conditioned with 2.5% (w/v) KOH solution at 80°C for different reaction times in the range 3–36 h. The adsorption of uranium on PP-g-AN-AO-KOH fabric increased logarithmically with the reaction time for alkaline treatment. From this result, the optimal reaction time for alkaline treatment of PP-g-AN-AO fabrics in terms of uranium adsorption capacity was found to be ≥12 h.

CONCLUSIONS

AN has been grafted onto PP fabric by photoirradiation-induced graft polymerization with BP as the photoinitiator. A concentration of AN ≤1.0M, a photoirradiation time of 2 h, and a reaction temperature of 60°C would seem to be optimal for the grafting of AN onto PP in terms of a stable degree of grafting. The grafted AN was effectively converted into AO by reacting with ≥5.0% (w/v) hydroxylamine solution of pH in the range 7.0–9.0 for ≥16 h at
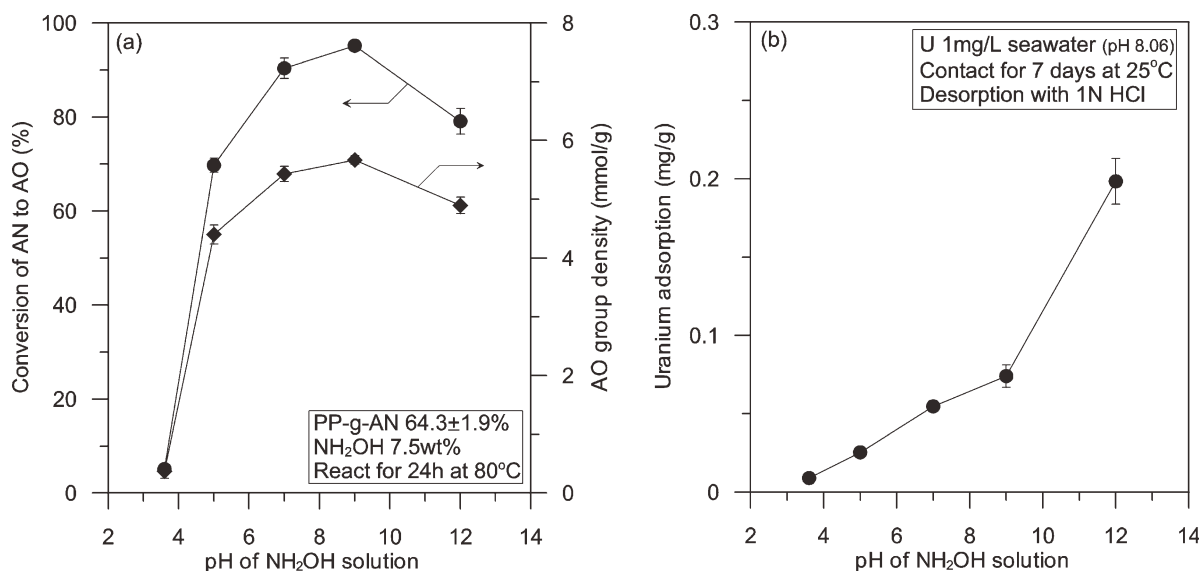
Figure 12 Effect of the pH of NH₂OH solution on the conversion ratio of AN to AO and the AN group density in the amidoximated fabric (a) and uranium adsorption capacity of the amidoximated fabric after conditioning with KOH (b).
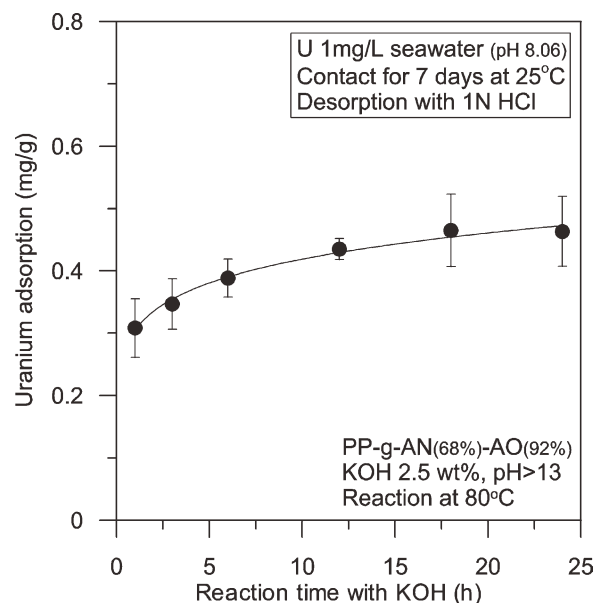
Figure 13 Effect of the reaction time with KOH for conditioning of the amidoximated fabric on the uranium adsorption capacity.

60–80°C. Under these conditions, $\geq 85\%$ of the grafted AN was converted into AO, regardless of the degree of AN grafting. The grafted AN and amidoximated AN-graft fabrics have been characterized by FTIR spectroscopy, SEM, and surface charge analysis. The conversion efficiency of AN to AO and the uranium adsorption capacity of the product indicated that methanol is not an essential solvent for the amidoximation reaction. Conditioning of the AO groups with KOH solution proved to be effective for enhancing the uranium adsorption capacity of amidoximated AN-grafted PP (PP-*g*-AN-AO) fabric, which increased logarithmically with the reaction time for conditioning. The optimal reaction time for conditioning PP-*g*-AN-AO fabric in terms of the uranium adsorption capacity would seem to be ≥ 12 h. The AO group density in PP-*g*-AN-AO fabric increased linearly with the degree of AN grafting. However, the uranium adsorption capacity of PP-*g*-AN-AO fabric conditioned with 2.5% KOH at 80°C for 24 h increased with the degree of grafting up to approximately 60% and then decreased with a further increase. This indicates that the optimal degree of AN grafting onto PP fabric for preparing an AO-containing sorbent that is effective in recovering uranium from seawater is 60%.

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