A mild method of amine-type adsorbents syntheses with emulsion graft polymerization of glycidyl methacrylate on polyethylene non-woven fabric by pre-irradiation

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ABSTRACT

A mild pre-irradiation method was used to graft glycidyl methacrylate (GMA) onto polyethylene (PE) non-woven fabric (NF). The polymer was irradiated by electron beam in air atmosphere at room temperature. The degree of grafting (D_g) was determined as a function of reaction time, absorbed dose, monomer concentration and temperature. After 30 kGy irradiation, with 5% GMA, surfactant Tween 20 (Tw-20) of 0.5% at 55 °C for 15 min, the trunk polymer was made grafted with a D_g of 150%. Selected PE-g-PGMA of different D_g was modified with aminated compounds such as ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA) and tetraethylenepentamine (TEPA). The obtained amine-type adsorbents were prepared to remove copper and uranium ions from solution. It was shown that at least 90% of copper and 60% of uranium with the initial concentration from 3 to 1000 ppb can be removed from water.

1. Introduction

Radiation induced graft polymerization is a well-known method for polymeric material modification (Saito et al., 1987; Tamada et al., 2004). After chemical modifications the resulting polymers were widely applied as metal ion adsorbents to recover rare metals such as uranium, scandium and heavy metals such as cadmium, copper, lead, etc. (Li et al., 1994; Seko et al., 2005). The most widely used precursor monomer for graft polymerization is glycidylmethacrylate (GMA), as the epoxy group can be modified easily into various functional groups (Saito et al., 2002; Hoshina et al., 2007). After a systematic study of the stability of GMA micelles in emulsion in the presence of surfactant, water can also be used as a solvent in emulsion polymerization instead of organic solvents (Seko et al., 2007, 2010). GMA was grafted onto numerous materials among which polyethylene (PE) and polypropylene (PP) are the most favorite matrix. However, most of the graft polymerization was carried out onto the copolymer of PE and PP because of the radiation crosslinking property of PE and radiation degradation property of PP. The usage of PE non-woven fabric (NF) is rarely reported as it is difficult to mould PE into NF in industry.

High D_g of GMA grafted PE fiber and PE/PP NF was reported at a relatively high dose of 200 kGy (Miyoshi et al., 2005; Iwanade et al., 2007). Besides, irradiation is usually carried out in a nitrogen atmosphere at very low temperature, which indeed prolonged the lifetime of the radicals and led to high D_g (Seko et al., 2007). It seems the technique of grafting has almost been mature. However, industrial application still calls for a mild method to reduce the costs. In this paper a method with high efficiency, easy handling and low cost possibilities was investigated. PE NF was irradiated in air atmosphere at room temperature with relative low dose of 30 kGy. Graft polymerization of GMA was carried out in an emulsion solution. D_g was determined as a function of reaction time, absorbed dose, monomer concentration and temperature. Selected PE-g-PGMA NF of different D_g was modified with aminated compounds. The main objective of the present work is to elucidate the mild technique of radiation-induced grafting of GMA on PE NF and consequently to provide the radiation utilization method for recovering rare metals and heavy metals from solution.

2. Experimental

2.1. Materials

PE NF was supplied from DuPont Company, USA. GMA was purchased from J&K Chemical Ltd. and was used without purification. Tw-20 was supplied by Shanghai Chemical Reagent Co., Ltd., China, and was used directly as the surfactant. Other reagents were of analytical grade and were used as received.

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2.2. Grafting and chemical modification

PE NFs were irradiated by EB at a voltage of 1.8 MeV and a current of 2 mA in air atmosphere at room temperature. After irradiation, the NFs were immersed in GMA emulsions. The emulsion of GMA with 0.5 wt% Tw-20 was stirred for 1 h and aerated with nitrogen gas for 15 min in advance. Graft polymerization of GMA was carried out by keeping the glass ampoule in a water bath at certain temperature. After a pre-determined period, the GMA grafted NFs were removed from the grafting solution, washed three times with distilled ethanol and then extracted

with acetone for 48 h to remove the homopolymer and residual monomer. After drying under reduced pressure, the amount of GMA grafted onto PE NFs was evaluated by D_g, which was defined as follows:

$$D_g \ (\%) = (W_i - W_0)/W_0 \times 100$$

where W_0 and W_i are the weights of the PE NFs and GMA grafted NFs in dry state.

The GMA-grafted PE NFs with various D_gs were modified with 50% (V/V) of EDA, DETA, TETA and TEPA in 1, 4-dioxane at 80 °C for 1 h.
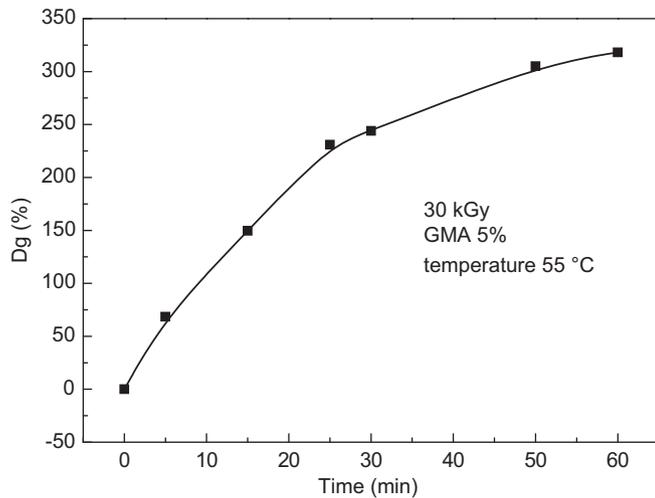

Fig. 1. Time course of GMA grafting on PE NFs. Dose: 30 kGy, GMA concentration: 5%, grafting time: 15 min and temperature: 55 °C.
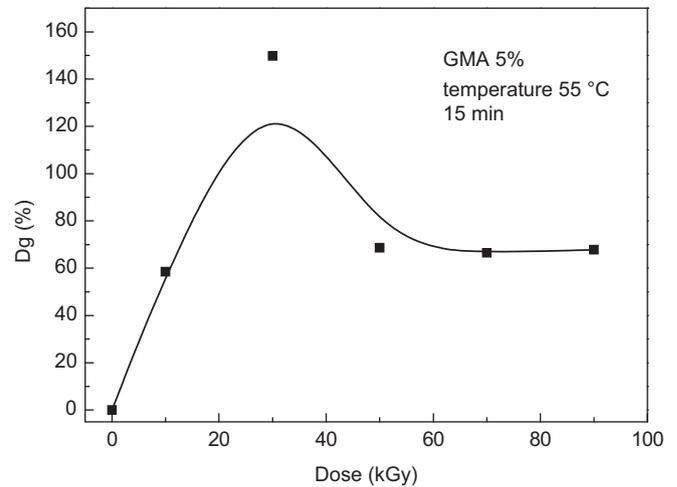

Fig. 3. Effect of pre-irradiation dose on D_g of PE-g-PGMA. GMA concentration: 5%, grafting time: 15 min and temperature: 55 °C.
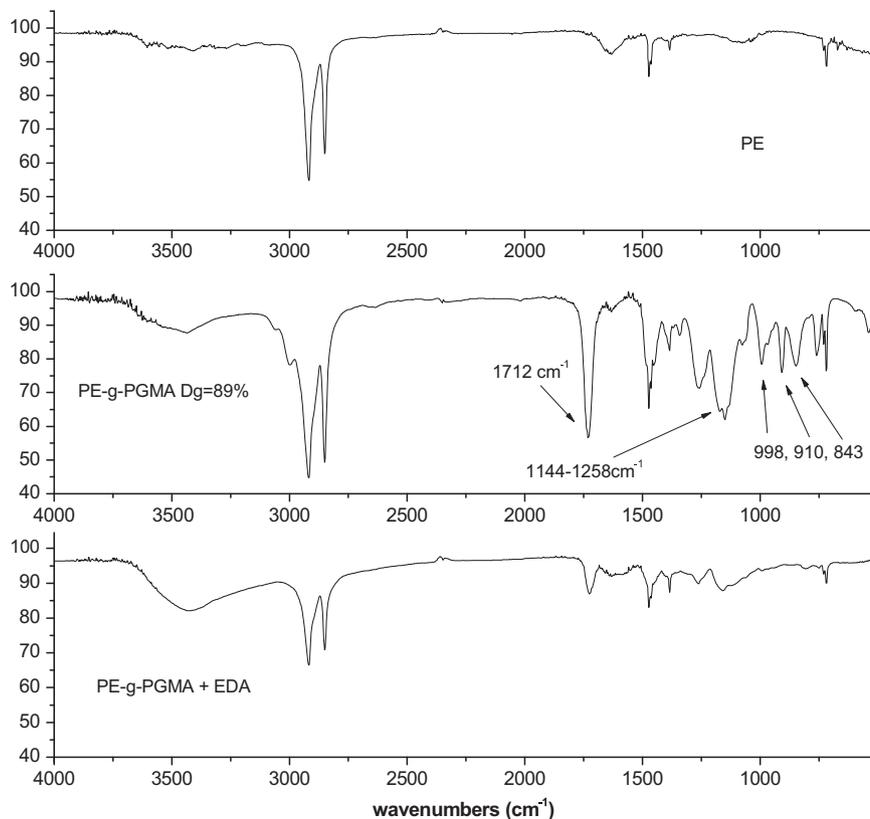

Fig. 2. FT-IR spectra showing PE, PE-g-PGMA and modified PE-g-PGMA with EDA.

Metal adsorption of the resulting adsorbent NFs was performed by batch adsorption. The removal ratio of metal ions was evaluated as follows:

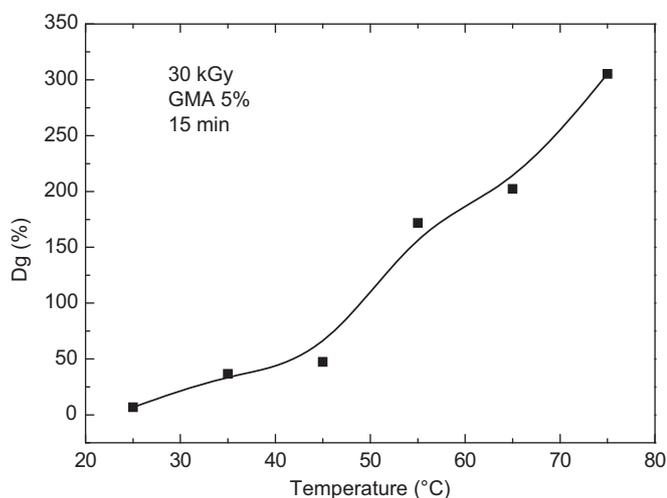Removal ratio $(\%) = (C_0 - C_i)/C_0 \times 100$

Fig. 4. Effect of grafting temperature on D_g of PE-g-PGMA. GMA concentration: 5%, dose: 30 kGy and grafting time: 15 min.

where C_0 and C_i are the concentrations of the metal ions in solution before and after adsorption, respectively. For the adsorption investigation of Cu^{2+}, 0.025 g adsorbents were soaked for 24 h in 50 ml 1 ppm Cu^{2+} solutions.

2.3. Analysis

The grafting of PE-g-PGMA was demonstrated by Fourier transform infrared (FT-IR) and differential scanning calorimetry (DSC). Images of the cross-section and surface of the material were taken on a scanning electron microscope (SEM). The concentrations of uranium ions and copper ions were determined by inductively coupled plasma mass spectrometer (ICP-MS).

3. Results and discussion

3.1. Graft polymerization study

Graft polymerization was carried out at 55 °C in aqueous emulsion of 5% GMA and 0.5 wt% Tw-20 since GMA micelle is quite stable in this condition (Seko et al., 2007). Fig. 1 shows the time conversion of D_g at absorbed dose of 30 kGy. D_g increased with grafting time and reached 150% after 15 min, gradually reached a platform of 320% after 60 min. Strong absorption at about 1712 cm^{-1} (C=O stretching) and 1144−1258 cm^{-1} (C—O— stretching) was
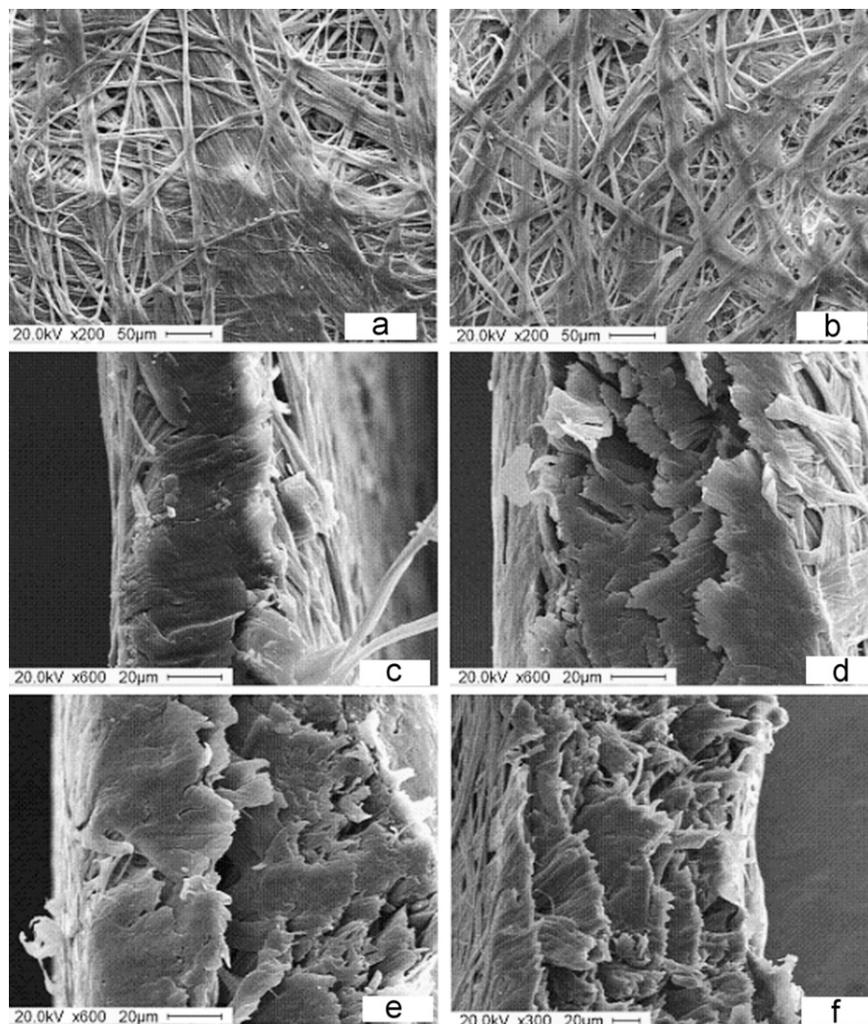

Fig. 5. SEM images of the surface of PE NF (a), PE-g-PGMA with D_g of 342% (b) and cross section of PE fabrics (c), PE-g-PGMA with D_g of 58% (d), (e) 89% and (f) 342%.

observed from the FTIR spectrum shown in Fig. 2. Besides, 998, 910 and 843 cm^{-1} represent the characteristic vibrations of epoxy groups, which clearly indicate that GMA was introduced onto PE NF.

PE NFs were irradiated at five different doses to investigate the effect of absorbed dose on D_g. Grafting was carried out in 5% GMA emulsion at 55 °C for 15 min. The results from Fig. 3 indicate that with the increasing of dose D_g increased and gradually reached a maximum at 30 kGy then decreased, and finally kept a constant value after 50 kGy. In the case of high dose irradiation, the rate of graft polymerization is too high that the simultaneous cross-linking in the PE NF would suppress the diffusion of GMA into the polymer (Seko et al., 2007).

Fig. 4 shows the effect of grafting temperature on D_g at the grafting time of 15 min in 5% GMA emulsion in the case of 30 kGy pre-irradiation. D_g increased with temperature and reached 170% at 55 °C. Further increase in grafting temperature led to a steep increment of D_g and the value was 300% at 75 °C. Based on this result we could presume that the temperature of 50 °C would be enough for the grafting reaction with 100% D_g and it is adequate for the preparation of metal ion adsorbents.

SEM images of the surface and cross sections of PE and PE-g-PGMA NFs are shown in Fig. 5. The surface section image (Fig. 5a) of the NF reveals the fiber morphology, criss-crossed by a network of fibers with $5-25$ μm in diameter. The surfaces remain almost the same with the increase in D_g beyond our expectations. In the view of patent protection we could not tell the specific treatment on the surface of the trunk NF. With the increment of D_g, the thickness of NF increased from 30 to 50 μm at the D_g of 89% and delamination was observed clearly. Meanwhile, NFs with higher D_g would become hard and gradually brittle. The melting temperature (T_m) and ΔH_f of the trunk NF and PE-g-PGMA of different D_g are summarized in Table 1. T_ms of the materials decreased indistinctly with the increase in D_g, while ΔH_f decreased sharply with the increase in D_g. At the beginning of grafting, the amount of the grafted side chain increased with the increment of D_g. Grafting takes place in the entire amorphous region without any significant disruption in the crystalline structure of NF and the decrease in the degree of crystallinity is mainly attributed to the dilution effect (Nasef, 2002).

Fig. 6 shows the effect of GMA concentration on D_g at the temperature of 55 °C after 15 min grafting in the case of 30 kGy pre-irradiation. Graft polymerization could proceed with 1% GMA and gave a D_g of 23%. At the concentration of 2.5% D_g became 130% and the maximum value was 150% with 5% GMA. This D_g is enough for precursor for application to metal ion adsorbent. The further increase in GMA concentration led to a decrease in D_g because of homopolymerization of the monomer.

3.2. Modification of PE-g-PGMA

Above results show the optimum condition to prepare PE-g-PGMA NFs. Then amine-type adsorbents were synthesized by reacting EDA, DETA, TETA and TEPA with the NFs. Fig. 2c shows

Table 1
T_m and ΔH_f of PE and PE-g-PGMA of different D_g from DSC data.

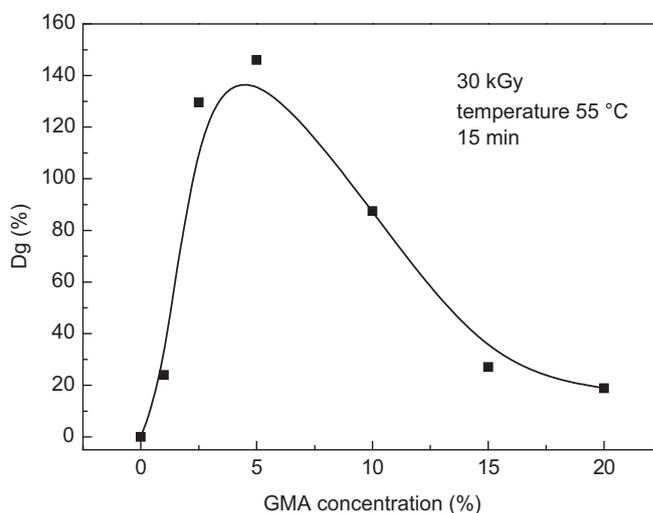| D_g (%)	T_m (°C)	ΔH_f (J g^{-1})
0	143.4	169.6
11	139.7	168.6
58	138.2	117.9
71	137.8	97.4
89	137.4	92.3
382	137.0	29.5
410	136.2	27.8

Fig. 6. Effect of monomer concentration on D_g of PE-g-PGMA. Temperature: 55 °C, dose: 30 kGy, grafting time: 15 min.
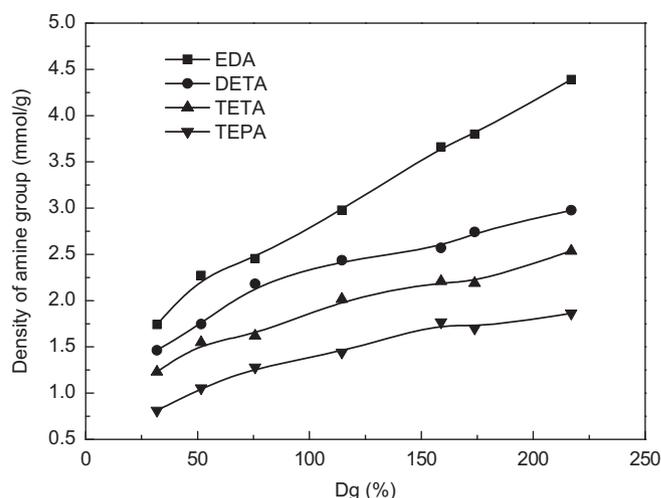

Fig. 7. Density of amine groups in EDA, DETA, TETA and TEPA type adsorbents.

the infrared spectra of the EDA modified PE-g-PGMA NFs. After modification the characteristic vibrations of epoxy groups at 998, 910 and 843 cm^{-1} disappeared. A broad band at about 3450 cm^{-1} (NH$_2$ stretching) appeared as the amine group was introduced into PE-g-PGMA. The density of amine group almost linearly depends on D_g and decreases along with the molecular weight of the amine compounds (Fig. 7). Seko and co-workers found that 150% D_g gave 4 mmol-epoxy groups in 1 g grafted-PE fibers (Seko et al., 2007), which are equivalent to that of commercially available adsorbent resin.

3.3. Absorptive property of modified adsorbents

The grafted NF with a D_g of 163% was treated by EDA and TETA, and the density of amine group in obtained NF was 4.56 and 2.88 mmol/g, respectively. Metal adsorption of the resulting adsorbent fibers was performed by batch adsorption of Cu and U ions. After soaking in 1 ppm Cu^{2+} solution for 24 h, EDA-type adsorbents could remove at least 90% Cu^{2+} ions from the solution. In the case of uranium ions, NaHCO$_3$ was used to adjust the pH value of the solution to 8.3 as the value of natural seawater remains stable at pH 7.9–8.4 with complex inorganic carbonate and bicarbonate. After 24 h adsorption with different initial concentrations from 3 to 1000 ppb, the removal ratio of uranium ions was listed in Table 2.

Table 2
Removal ratio of U ions in two solutions with two adsorbents (PE-g-PGMA D_g 195%).

U (ppb)	Removal ratio (%)			
Solution	Pure uranyl nitrate solution		Uranyl nitrate solution with NaHCO$_3$ (pH=8.3)	
Adsorbents-type	EDA	TETA	EDA	TETA
3	91.5	87.6	42.9	48.7
10	96.4	96.1	74.0	69.3
100	90.5	89.2	65.2	61.1
1000	77.5	71.9	64.2	60.1

Obviously, the adsorbents show higher absorption capability in pure uranyl nitrate solution than that in bicarbonate solution. When the concentration of U is 3 ppb, the removal ratio of uranium ions is almost 90% in pure uranyl nitrate solution. While only 50% of uranium ions can be removed from the bicarbonate solution. The removal ratio did not decrease until the concentration of U was increased to 1000 ppb, in which case the removal ratio became 75% in pure uranyl nitrate solution and 62% in the bicarbonate solution. Besides, the absorptive property of EDA-type adsorbent was a little higher than that of TETA-type against U ion.

4. Conclusions

Under the irradiation by electron beam in air atmosphere at room temperature, PE NF was grafted by GMA with high D_g. This is an improvement to the traditional method. The obtained PE-g-PGMA of different D_g was modified with amine-type compounds. The density of amine group in EDA, DETA, TETA and TEPA type

adsorbents is high enough to be used as adsorbents of copper and uranium ions from water. It was shown that at least 60% of uranium with the initial concentration from 3 to 1000 ppb can be removed from water.

References

Hoshina, H., Seko, N., Ueki, Y., Tamada, M., 2007. Synthesis of graft adsorbent with N-methyl-D-glucamine for boron adsorption. Journal of Ion Exchange 18, 236–239.

Iwanade, A., Umeno, D., Saito, K., Sugo, T., 2007. Protein binding to amphoteric polymer brushes grafted onto a porous hollow-fiber membrane. Biotechnology Progress 23, 1425–1430.

Li, G.Q., Konishi, S., Saito, K., Sugo, T., 1994. High collection rate of Pd in hydrochloric acid medium using chelating microporous membrane. Journal of Membrane Science 95, 63–69.

Miyoshi, K., Saito, K., Shiraishi, T., Sugo, T., 2005. Introduction of taurine into polymer brush grafted onto porous hollow-fiber membrane. Journal of Membrane Science 264, 97–103.

Nasef, M.M., 2002. Structural investigation of polystyrene grafted and sulfonated poly(tetrafluoroethylene) membranes. European Polymer Journal 38, 87–95.

Saito, K., Saito, K., Sugita, K., Tamada, M., Sugo, T., 2002. Convection-aided collection of metal ions using chelating porous flat-sheet membranes. Journal Chromatography A 954, 277–283.

Saito, K., Yamada, S., Furusaki, S., Sugo, T., Okamoto, J., 1987. Characteristics of uranium adsorption by amidoxime membrane synthesized by radiation-induced graft polymerization. Journal of Membrane Science 34, 307–315.

Seko, N., Tamada, M., Yoshii, F., 2005. Current status of adsorbents for metal ions with radiation grafting and crosslinking technique. Nuclear Instrument and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 236, 21–29.

Seko, N., Bang, L.T., Tamada, M., 2007. Synthesis of amine-type adsorbents with emulsion graft polymerization of glycidyl methacrylate. Nuclear Instrument and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 265, 146–149.

Seko, N., Thi Yen Ninh, N., Tamada, M., 2010. Emulsion grafting of glycidyl methacrylate onto polyethylene fiber. Radiation Physics and Chemistry 79, 22–26.

Tamada, M., Seko, N., Yoshii, F., 2004. Application of radiation-graft materials for metal adsorbent and crosslinked natural polymer for healthcare products. Radiation Physics and Chemistry 71, 223–227.