

Synthesis of Amine-Type Adsorbents with Emulsion Graft Polymerization of 4-Hydroxybutyl Acrylate Glycidylether

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ABSTRACT

Radiation induced graft polymerization on polymeric matrix followed by functionalization is widely accepted for the preparation of metal adsorbents. In this paper, a pre-irradiation method was used for emulsion graft polymerization of 4-hydroxybutyl acrylate glycidylether (4-HB) onto polyethylene/polypropylene (PE/PP) nonwoven fabric. The degree of grafting (D_g) which can be calculated by weight increment was determined as a function of reaction time, irradiation dose, and monomer concentration. After 30 kGy irradiation, with 4-HB concentration of 5%, surfactant Span 20 of 0.5% at 40°C for 2 h, the trunk polymer was made grafted at a D_g of 135%. 4-HB-grafted PE/PP nonwoven fabric was modified by ethylenediamine (EDA) in isopropyl alcohol (IPA) as a solvent at 60°C. With a D_g of 135%, the amine group density of the adsorbent is 2.8 mmol/g. The adsorption test was carried out by batch experiment in several metal ion solutions, and the removal ratio from the EDA modified adsorbent of the metal ions is in the order of $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Li}^+$. Compared with glycidyl methacrylate (GMA) which is a typical functional monomer for graft polymerization, 4-HB-grafted adsorbent exhibited not only better mechanical property but also higher adsorption capacity of Cu^{2+} and Pb^{2+} .

Keywords: Graft Polymerization, Pre-irradiation, 4-hydroxybutyl Acrylate Glycidylether (4-HB), Glycidyl methacrylate (GMA), Amine-Type Adsorbent

1. Introduction

Aquatic pollution by heavy metals has attracted worldwide attention for many decades. Several heavy metals such as cadmium, chromium, copper, lead, mercury, nickel, zinc, etc. are included on the U.S. Environmental Protection Agency's (USEPA) list of priority pollutants [1]. Copper is an essential micronutrient, vital for the body in small amounts. However, humans can present symptoms from temporary stomach and intestinal disorders to kidney or liver damage at high amount over 1.3 $\text{mg}\cdot\text{dm}^{-3}$ [2]. Lead intoxication has been a problem throughout history [3,4], adverse health effects of lead are well documented: it may cause severe damage to the kidney, nervous system, reproductive system, liver and brain and causes sickness or death [4,5]. The permissible limits for lead in drinking water given by USEPA are 0.015 $\text{mg}\cdot\text{dm}^{-3}$ [6] and for wastewaters is 0.1 $\text{mg}\cdot\text{dm}^{-3}$ given by both USEPA and Bureau of Indian Standards

(BIS) [7,8]. The potential sources of Cu^{2+} ions are, essentially, pulp, paper and wood preservative-employing mills, industrial waste streams of metal cleaning and plating baths, fertilizer industry, *et al.* [9]. Lead has been used for many years in products of everyday life (paint, household plumbing, water pipes and *et al.* [10-12]. Hence, both Cu^{2+} and Pb^{2+} ions are ubiquitous and frequently found toxic metals in surface water. And it becomes mandatory for the removal of lead from drinking and wastewaters. Therefore, several processes have been used and developed over years to remove such metals from industrial wastewater: biological process [13-15], ion exchange [16], membrane filtration [17,18], adsorption or electrochemical recovery [19,20] *et al.* For the adsorption task, both inorganic [21,22] and organic especially polymeric materials [23] have been explored successfully for years. Many techniques have been suggested in the literature for the synthesis of polymeric

adsorbents [24,25].

The widespread interest in radiation-induced graft polymerization has largely been driven by the benefits of economical, clean and efficient. Under the irradiation of high-energy sources such as γ -ray or electron-beam, free radicals were generated in the polymeric material and these free radicals initiated the graft polymerization of the monomers (**Figure 1**). Therefore, polymeric grafts were covalently connected to the raw material, which can impart the raw material with desirable properties [26-30]. After chemical modifications the resulting polymers were widely applied for preparation of metal adsorbents to recover rare metals such as uranium recovery from seawater, rare metals from hot spring water, cadmium from scallop and *et al.* [26,31-33].

For the past decades glycidylmethacrylate (GMA) is considered to be the most widely used precursor monomer for graft polymerization, as the epoxy group can be modified easily into functional groups [34-36]. However, too much high D_g would lead the brittleness of grafted material. Hence, 4-hydroxybutyl acrylate glycidylether (4-HB) was used to synthesize the metal ion adsorbent. 4-HB shares the similar molecular structure with GMA with an epoxy group at the end. The extra 4 methylene group of 4-HB makes the molecular structure longer than GMA (**Figure 1**). Therefore, the graft polymerization process and the absorptive property of modified adsorbents should be investigated.

In this paper the PE/PP nonwoven fabric (NF) was irradiated with electron beam in N_2 atmosphere at dry ice temperature. Graft polymerization of 4-HB was carried out in emulsion in order to find the optimum conditions to prepare grafted PE/PP-g-P4-HB material. The degree of grafting (D_g) was determined as a function of irradiation dose, monomer concentration and reaction time. Taking account of the high affinity of N and S donor

containing ligands for metal ions such as Cu^{2+} , Pb^{2+} , Zn^{2+} , Ni^{2+} [36], the selected PE-g-PGMA was modified with ethylenediamine (EDA). The main aim of this article is to elucidate the mild technique of radiation-induced graft polymerization of 4-HB on PE/PP NF and consequently to explore the feasibility of the radiation utilization method for recovering heavy and rare metals.

2. Experimental

2.1. Materials

Trunk material of nonwoven fabric (NF) composed of polyethylene-coated polypropylene (Kurashiki MFG Co., Osaka, Japan) was used as a trunk polymer for graft polymerization. 4-HB and GMA was purchased from Tokyo Kasei Kogyo Co. Ltd., Japan, and used without further purification. Ethylenediamine (EDA), sodium n-dodecyl sulfate (SDS), polyethylene glycol (PEG), sorbitan monolaurate (Span 20), polyoxyethylene sorbitan monolaurate (Tween 20), polyoxyethylene sorbitan palmitate (Tween 40), and polyoxyethylene sorbitan monostearate (Tween 60) and isopropyl alcohol (IPA), were purchased from Kanto Chemical Co., Ltd. Copper, lead, zinc, nickel, lithium standard solution for quantitative analysis (1000 ppm) and ultrapure nitric acid (ultrapure-100) were purchased from Kanto Chemical Co., Ltd. Potassium hydroxide were of analytical grade and used as received. Other chemicals of reagent grade such as methanol (MeOH) and water from a Milli-Q purification system were used in washing treatments.

2.2. Preparation of 4-HB Emulsion Solution

An amount of 4-HB with certain surfactant such as SDS, PEG, Span 20, Tween 20, Tween 40 and Tween 60 were added into the water solution. The solution was mixed with a homogenizer at room temperature for 5 min to get

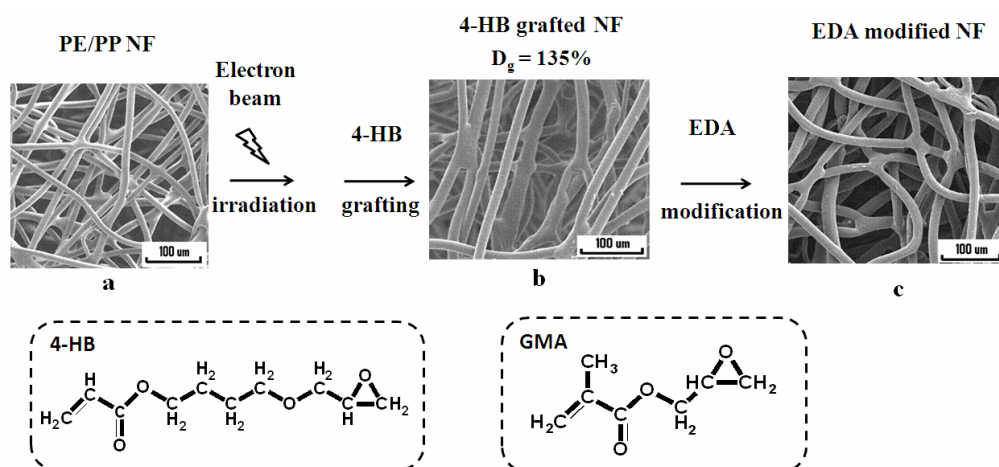


Figure 1. Preparation scheme of amine type adsorbent.

a homogeneous emulsion state. The micelle size of 4-HB/Span 20 was evaluated by fiber optics dynamic light scattering spectrophotometer (FDLS-3000, Otsuka Electronics, Co. Ltd., Japan).

2.3. Graft Polymerization and Chemical Modification

The NF in long sheet was cut into 3 cm × 7 cm square pieces which were then packed into polyethylene bags. After the replacement of the air in the polyethylene bag by nitrogen gas, the NF pieces were cooled at dry-ice temperature and exposed to an electron beam irradiation. The irradiated NF pieces were transferred to a glass ampoule and the air inside was evacuated to remove O₂. Then, an aqueous emulsion containing 4-HB and Span 20 was drawn into the glass ampoule via suction. Graft polymerization of 4-HB was carried out by keeping the glass ampoule in a water bath at 40°C. After the graft polymerization, the grafted NF pieces were washed three times with methanol and dried. After drying under the reduced pressure, the amount of 4-HB grafted onto NF was evaluated by the degree of grafting (D_g). D_g was defined as follows:

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

where, W₀ is the initial weight of NF and W_i weight of NF after graft polymerization.

4-HB-grafted NF was aminated by 70% EDA in IPA at 60°C to introduce the adsorption unit [37]. After 3 h reaction, the 4-HB-grafted NF was taken out from the solution, washed with distilled water. After drying under reduced pressure, the density of amine group of the adsorbent was estimated by:

$$\text{Amine group density (mmol/g-adsorbent) (\%)} = (Z_i - Z_0) / Z_i / M \times 100,$$

where, Z₀ and Z_i are the weights of 4-HB-grafted NF before and after chemical modification and M the molecular weight of the EDA.

2.4. Metal Adsorption

Metal adsorption of the amine type adsorbent fabrics was performed by batch adsorption. 0.02 g EDA modified NF was soaked in 45 ml of metal ions of 10 ppm. The removal ratio of metal ions was evaluated as follows:

$$\text{Removal Ratio (\%)} = (C_0 - C_i) / C_0 \times 100,$$

where, C₀ and C_i are the concentrations of the metal ions in solution before and after adsorption.

2.5. Analysis

The graft polymerization of 4-HB-grafted NF was demonstrated by Fourier transform infrared (FT-IR) in a transmittance mode on a PerkinElmer Spectrum One FT-IR. The NF before and after graft polymerization was

observed with a scanning electron microscope (SEM, Hitachi SEMDX Type N) after sputtered with gold. The concentration of the remaining metal ion was measured by optical emission spectrometer (Optima 4,300 DV).

3. Results and Discussion

3.1. Emulsion Stability

In order to get suitable graft polymerization condition the stability of 4-HB emulsion solution prepared by several different surfactants was investigated to optimize the grafting condition. 5 wt% of 4-HB was added into 1 wt% certain surfactant water solution. The resulting emulsions of 4-HB with surfactant were in a milky state with different size of micelle after high speed magnetic stir by a homogenizer. For a stable emulsion not only the milky state but also the size of micelle should keep constant all along and their stabilities of homogeneous emulsions states were summarized in **Table 1**. In the case of SDS and PEG the emulsion could not maintain a milky state and separated into layers within half an hour. Milky state prepared with Tween's maintained for 6 h and then gradually changed into separated layers (**Figure 2(d)**). The most stable emulsion of 5 wt% 4-HB in water was obtained with the addition of Span 20, in which the milky state can keep for at least 24 h (**Figure 2**). In order to optimize the state of 4-HB/Span 20 emulsion, the concentration of Span 20 was changed and the result was shown in **Figure 3**. Obviously, the size of micelle increased from 200 to 600 nm when the concentration of Span 20 was reduced from 1.0 to 0.1 wt%. Therefore, the optimal emulsion of 4-HB was obtained when the concentration of Span 20 was set at 0.5 wt%.

3.2. Graft Polymerization

The NF was irradiated at five different irradiation doses: 10, 20, 30, 40 and 50 kGy to investigate the effect of irradiation dose on D_g. The emulsion graft polymerization was carried out at 40°C in the aqueous emulsion of 5% 4-HB and 0.5% Span 20. **Figure 4** depicts the D_g of 4-HB onto the NF as a function of irradiation dose after 1 h. The results indicated that the D_g of 4-HB increased linearly with the increase of the absorbed dose below 40 kGy. Grafting saturation with a D_g of 180% was achieved at

Table 1. Stability of 4-HB emulsion prepared by different surfactants.

Surfactant	Stability of milky state
SDS	<0.5 h
PEG	<0.5 h
Span 20	24 h
Tween 20	6 h
Tween 40	6 h
Tween 60	6 h

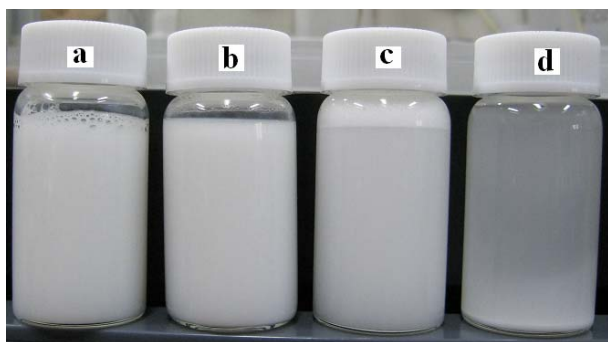


Figure 2. Milky state of the emulsion prepared with Span 20 (a), keep for 48 h (b), Tween 20 (c), and keep for 24 h (d).

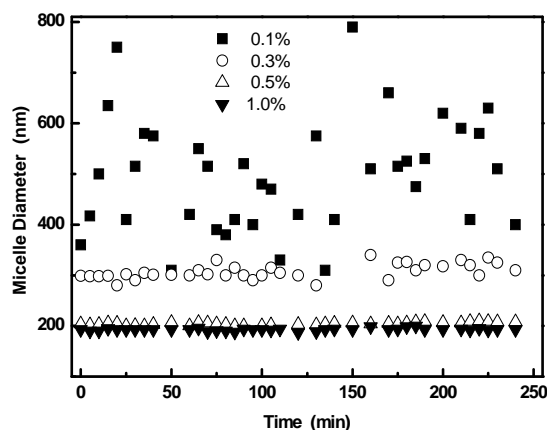


Figure 3. Micelle diameter at various concentrations of Span 20, (■) 0.1%, (○) 0.3%, (△) 0.5% and (▼) 1.0%.

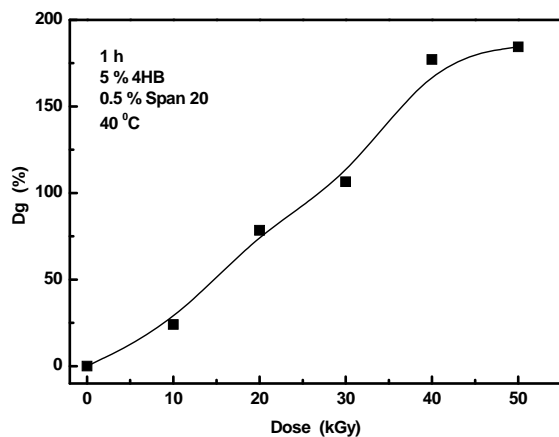


Figure 4. Effect of pre-irradiation dose on D_g , with 5% 4-HB, 0.5% Span-20 at 40 °C after 1 h grafting.

50 kGy. It is well known that pre-irradiation induced graft copolymerization relies heavily on the amount of trapped radicals generated in the trunk polymer. The linearly increased D_g is due to the amount of efficient trapped radicals with the dose increment, which is accompanied by an increment in the initiation, followed by

predominance in propagation and suppression in termination [38]. However, as already reported in literature, once the rate of graft polymerization is too high to exceed the diffusion rate of monomer into the fabric, the simultaneous cross-linking in the fabric suppresses the diffusion of 4-HB into polyethylene [39]. Hence, pre-irradiation dose below 50 kGy is considered to be favorable for 4-HB graft polymerization onto PE/PP NF.

Figure 5 shows the effect of 4-HB concentration on D_g in the case of 50 kGy pre-irradiation at 40 °C after fixed time interval of 0.5, 1, 2, 3 and 4 h. Set grafting time of 1 h for example, a concentration of 2.5% 4-HB yielded a D_g of 60%. At the concentration of 5% the D_g reached 175% which is enough for precursor for application to metal ion adsorbent [39]. Then the increase of concentration led a slower increment and gave a platform value of 290% at the concentration of 15%. The further increase of 4-HB concentration would result in a homo-polymerization, which turned out to be uneconomical and unnecessary. Evidence from the above suggests a concentration of 5% 4-HB would be appropriate for this graft polymerization.

Figure 6 shows the time conversion of D_g at 40 °C in the aqueous emulsion of 5% 4-HB at pre-irradiation dose of 30 and 50 kGy, respectively. At pre-irradiation dose of 50 kGy, D_g increased drastically with grafting time and reached 130% after 30 min, and gradually leveled off after 3 h with a D_g of 280%. As the diffusion rate of the monomer to the internal radicals in the polymer substrate was impeded by graft polymerization and homo-polymerization, and eventually resulted in a certain value of D_g . At pre-irradiation dose of 30 kGy, D_g increased steadily with grafting time and reached 130% after 2 h. As a D_g of 130% is enough for precursor for application to metal ion adsorbent, it is more economical and easier to control the D_g at the dose of 30 kGy rather than 50 kGy.

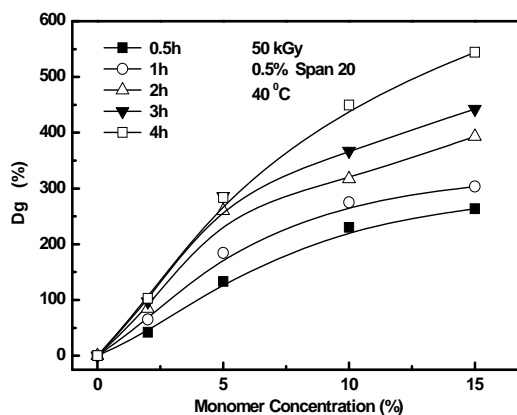


Figure 5. Effect of monomer concentration on D_g , after 50 kGy irradiation with 0.5% Span20 at 40 °C, (■) 0.5 h, (○) 1 h, (△) 2 h, (▼) 3h and (□) 4 h.

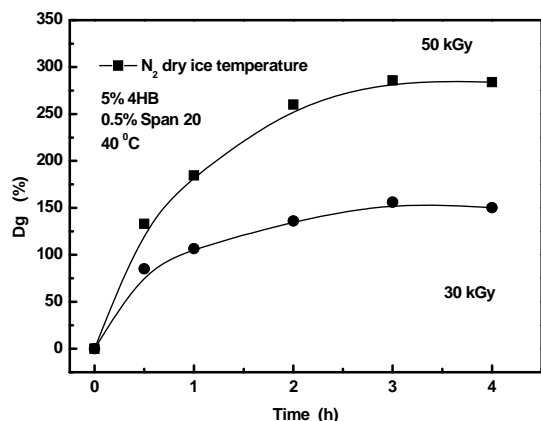


Figure 6. Time course of 4-HB grafting on NF, (■) 50 kGy and (●) 30 kGy irradiation dose.

The graft polymerization of NF with 4-HB was demonstrated by FT-IR. An example of a spectrum is given in **Figure 7** together with a spectrum of the trunk polymer. After the NF was grafted with 4-HB, the strong absorption at about 1726 cm^{-1} (C=O stretching) and 1251 cm^{-1} (-C-O- stretching) were observed. Besides, 847 cm^{-1} represented the characteristic vibrations of epoxy groups. Meanwhile, the characteristic vibrations of the carbonyl group increased with the increase of D_g . These results indicate that the introduction of poly-4-HB onto PE/PP fabric is clearly produced.

The SEM images of the surface sections of trunk NF and grafted material are shown in **Figure 1**. The surface section image of the fabric revealed the fiber morphology, crisscrossed by a network of fibers with $10\text{ }\mu\text{m}$ in di-

ameter (**Figure 1(a)**). After graft polymerization, the diameter of the fiber was doubled to $20\text{ }\mu\text{m}$ at the D_g of 130% (**Figure 1(b)**). In our previous study, the soft trunk NF became hard after grafted with GMA and then turned to brittle at a high D_g of 100%. However the 4-HB grafted-type material can keep soft even at a high D_g of 280%. The tensile curves are displayed in **Figure 8**, in which the three curves followed the similar propensity but with some discrepancy. From tensile strength and breaking elongation of single NF it is clearly that the GMA grafted NF can easily be broken under tension compared with 4-HB grafted one. When compare the molecular structure of 4-HB with GMA depicted in **Figure 1** the reason can be presumed as the 4 methylene groups of 4-HB. This subtle distinction makes the molecular structure of monomer flexible, further makes the side chain of polymer longer and flexible during the process of graft polymerization. Accordingly, not only the physical properties such as topography and mechanical properties of the grafted material but also their capability were improved, which will be elaborated below.

3.3. Modification of PE-g-P4-HB

All above results show that the optimum conditions to prepare 4-HB-grafted NF have been achieved by using relatively low irradiation dose at 30 kGy, low monomer concentration of 5%. And then amine-type adsorbents were synthesized by reaction of EDA with 4-HB grafted NF. **Figure 7c** shows the infrared spectra of the grafted NF with EDA group contents. As compared to the spectrum of the unmodified copolymers (**Figure 7(b)**), the

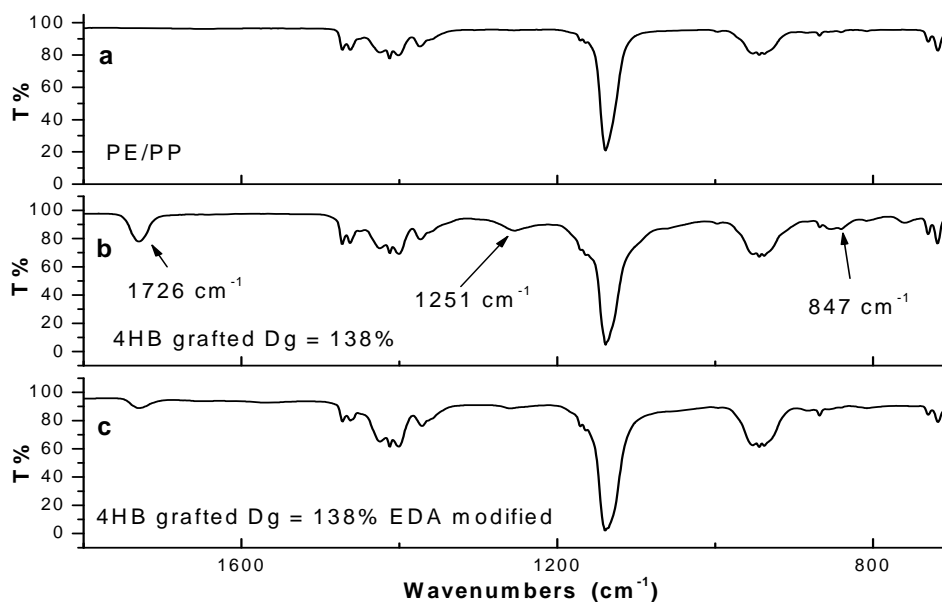


Figure 7. FT-IR spectra of NF, 4-HB-grafted NF and modified 4-HB-grafted NF with EDA.

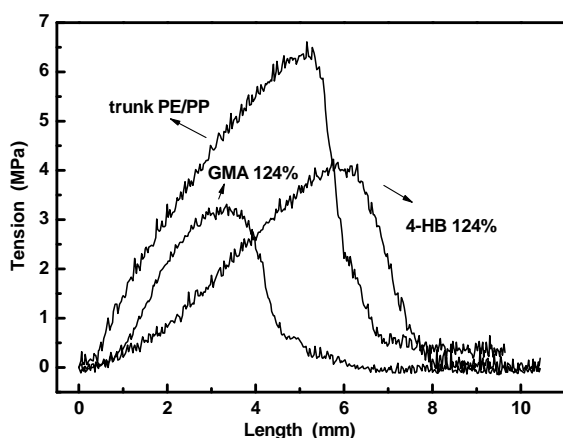


Figure 8. The typical tensile curves of NF, 4-HB-grafted NF and GMA-grafted NF.

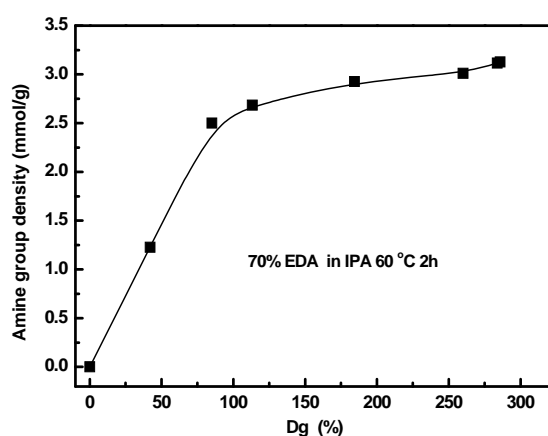


Figure 9. The density of amine groups in EDA-type adsorbents after 2 h modification at 60 °C.

characteristic vibrations of epoxy groups at 847 cm^{-1} disappeared because of the ring opening reaction. The density of amine group in EDA modified NF with different D_g were shown in **Figure 9**. In the case of material with low D_g the density of amine group almost linearly depended on the D_g , which also indicated that amine group could easily be introduced into grafted poly-4-HB. After modification, a D_g of 100% 4-HB-grafted NF yielded 2.5 mmol-epoxy groups in 1 g grafted material. The density of amine group preserved increasing but the ratio slowed down distinctly and finally reached a plateau value of 3.0 mmol/g at the D_g of 290%. In the SEM image shown in **Figure 1** the modified material seemed similar with the unmodified NF, which means no trail of destruction happened during the modification process.

3.4. Absorptive Property of Modified Adsorbents

The grafted NF with a D_g of 135% was treated by EDA at the optimized condition of modification, and the density of amine group was 2.8 mmol/g. Metal adsorption of the resulting adsorbent NF was performed by batch adsorption of 10 ppm metal ions. The absorptive behavior of the material depended on the pH value of the solution (**Figure 10**). Generally, the removal ratio of the metal ions increased with the increment of pH value and reached a platform of 95% for Cu^{2+} , 82% for Pb^{2+} and 73% for Zn^{2+} respectively at pH 5 after 5 h adsorption. The capability of this EDA modified NF was also studied in Ni^{2+} and Li^+ solutions. However, the removal ratio was very low. After 24 h, removal ratio of Ni^{2+} at pH 5 was only 23% (**Figure 11**). In the case of Li^+ , EDA modified NF was almost impotent (**Figures 10, 11**). Hence, the removal ratio of the EDA modified adsorbent is in the order of $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Li}^+$.

When compare the capability of 4-HB-grafted material with GMA-grafted one, certain D_g was designed before

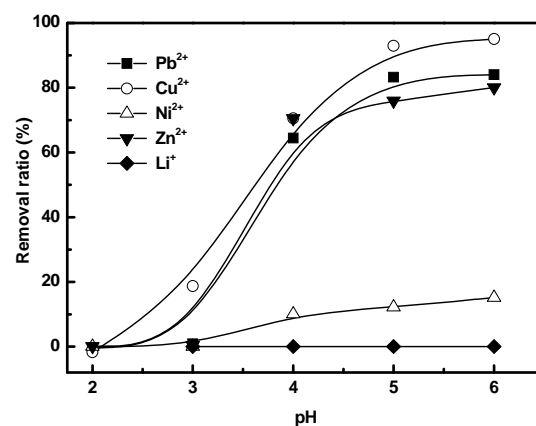


Figure 10. Removal ratio of metal ions at different pH values, (■) Pb^{2+} , (○) Cu^{2+} , (Δ) Ni^{2+} , (▼) Zn^{2+} and (◆) Li^+ .

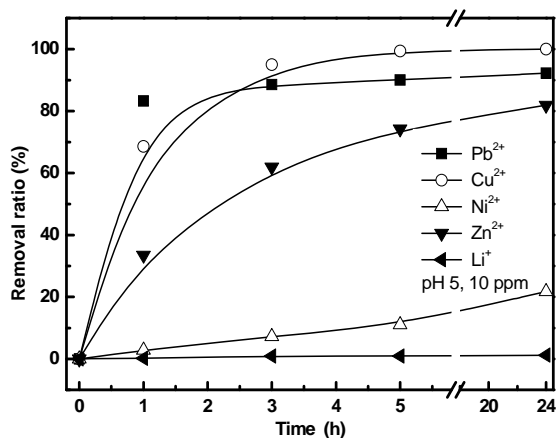


Figure 11. Removal ratio of metal ions with initial concentration of 10 ppm at pH 5, (■) Pb^{2+} , (○) Cu^{2+} , (Δ) Ni^{2+} , (▼) Zn^{2+} and (◄) Li^+ .

hand in order to control the density of amine groups. After treated by EDA the 4-HB-grafted NF with a D_g of

135% had an EDA density of 2.8 mmol/g. The conversion of epoxy group was more than 95%. In the case of GMA, a D_g of 100% gave an EDA density of 3.0 mmol/g. As displayed in **Figure 12**, the different molecular structure of 4-HB and GMA led different side chain of the polymer and eventually resulted in different absorptive capability of metal ions. After 3 days' adsorption, the removal ratio of Cu^{2+} and Pb^{2+} from both 4-HB and GMA grafted material could reach more than 95%. However, for both Cu^{2+} and Pb^{2+} the removal ratio from the 4-HB-grafted material increased more rapidly than the GMA-grafted as time went on (**Figure 12**). Especially for Cu^{2+} , after 5 h adsorption 4-HB-grafted material showed a removal ratio of about 90%, while the GMA-grafted one only 60%. As mentioned above, the 4 methylene groups of 4-HB make the side chain longer and flexible. Hook shaped functional groups on the side chain stands for the chelation of metal ions. With the long and flexible side chain, the mobility of the amine functional groups is enhanced and it is easier to catch the target ion. For the radius of a single ion, Pb^{2+} is much larger (0.120 nm) than Cu^{2+} (0.072 nm). Hence, the adsorption rate of the 4-HB-grafted is higher than that of the GMA-grafted, especially for the smaller ions of Cu^{2+} . After soaking in the 10 ppm solution for 5 h, the 4-HB-grafted adsorbent presented a removal ratio of 96% for Cu^{2+} and 93% for Pb^{2+} , respectively. That means the selectivity of Cu^{2+} is slightly higher than that of Pb^{2+} . However, in the case of GMA-grafted, after 5 h adsorption the removal ratio for Cu^{2+} is only 60% and for Pb^{2+} is 93%. That means the selectivity of Pb^{2+} is much higher than that of Cu^{2+} . As a consequence, the less soft GMA-type material can catch the bigger Pb^{2+} ion efficiently. Subtle distinction of 4 methylene groups of 4-HB gave birth to a remarkable progress of not only mechanical

property but also higher adsorption capacity. Relevant theoretical research is now continuing and the detail of the mechanism is expected in the next paper.

4. Conclusions

4-HB can be grafted onto NF with a pre-irradiation method. Stable emulsion of 4-HB was prepared with 0.5 wt% Span 20 in water. The optimum conditions to prepare 4-HB-grafted NF have been achieved by using relatively low irradiation dose at 30 kGy, low monomer concentration of 5% with the surfactant of 0.5% Span 20 at 40°C. After 2 h, the trunk polymer is made grafted at a D_g of 135%. 4-HB-grafted NF was modified by EDA in IPA as a solvent at 60°C. With a D_g of 135%, the adsorbent shows an amine group density of 2.8 mmol/g. The adsorption test was carried out by batch experiment in several metal ion solutions, and the removal ratio from the EDA modified adsorbent of the metal ions is in the order of $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Li}^+$. The removal ratio of the metal ions increased with the increment of pH value and reached a platform of 95% for Cu^{2+} , 82% for Pb^{2+} and 73% for Zn^{2+} at pH 5 after 5 h adsorption in 10 ppm metal ion solutions. After 24 h, the removal ratio of Ni^{2+} at pH 5 was only 23%, and Li^+ cannot be removed from the solution. Compared with GMA, subtle distinction of 4 methylene groups of 4-HB gave birth to a remarkable progress of the material. The longer side chain makes the material more flexible. Hence, 4-HB-grafted adsorbent exhibited not only better mechanical property but also higher adsorption capacity when it is used to remove Cu^{2+} and Pb^{2+} from solution. The long methylene unit would be a promising improvement of the adsorbents.

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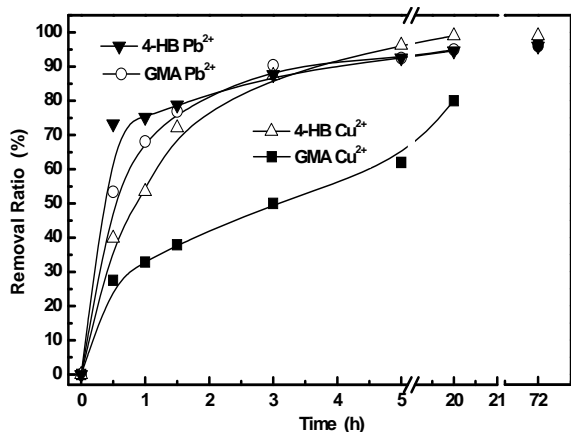


Figure 12. Removal ratio of metal ions from (■) GMA-grafted NF for Cu^{2+} , (○) GMA-grafted NF for Pb^{2+} , (Δ) 4-HB-grafted NF for Cu^{2+} and (▼) 4-HB-grafted NF for Pb^{2+} .

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