Crosslinking Induced by Irradiation Raises Selectivity of Polymeric Adsorbent

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ABSTRACT: Amine-type adsorbents were prepared by radiation-induced graft polymerization. The sorption behaviors for an individual metal ion of Cu^{2+} and Pb^{2+} separately, as well as with mixed Cu^{2+}/Pb^{2+}, were studied in both column and batch mode. Ethylenediamine-type adsorbent exhibited a high capacity for Cu^{2+} and Pb^{2+} at a high flow rate of 1000 h^{-1}, but low selectivity in the mixed Cu^{2+}/Pb^{2+} solutions. Radiation-induced crosslinking of the amine-type adsorbent was performed in water to improve selectivity. Crosslinking of the material was demonstrated by gel fraction, water content, and scanning electron microscopy image. Compared with the results from the noncrosslinked adsorbents, the breakthrough curve of Cu^{2+} right shifted, whereas the breakthrough curve of Pb^{2+} left shifted, indicating the higher adsorption capacity of Cu^{2+} and the lower adsorption capacity of Pb^{2+} from the crosslinked adsorbent. After 300 kGy irradiation, the crosslinked adsorbent was found to selectively adsorb Cu^{2+} from the mixed Cu^{2+}/Pb^{2+} solution. The results revealed that crosslinking raised the selectivity of the adsorbents. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 128: 4253–4260, 2013

INTRODUCTION

Radiation-induced graft polymerization is a mature technique that has been used for decades to modify a variety of matrices and further used in environmental and biotechnological applications.[1–3] For environmental remediation, it is well accepted that metal ions such as Cu, Pb, Zn, and Fe, among others, can be immobilized by chelation with a N, O, or S donor-containing ligand groups which are covalently attached to a polymer matrix.[4] A variety of metal ion adsorbents can be prepared by introducing the chelating function groups to trunk polymers such as polyethylene (PE), polypropylene (PP), and so on (Schemes 1 and 2). Thus, this attracted considerable interest in the field of rare metal and heavy metal recovery, such as of uranium from seawater, scandium from hot spring water, cadmium from scallops, and so on.[5–8] Widespread use in environmental remediation, however, has been limited by the difficulty in obtaining a desirable combination of high selectivity and high capacity. The extent of metal-ion adsorption by chelating groups may be expressed in terms of the metal ion itself and by the intrinsic adsorbability of these chelating groups. Generally speaking, the selectivity of one type of adsorbent is relatively low. Taking the most common lone-pair electron-donating atom N, for example, as many metal ions have high affinity to

N, amine-type adsorbents show low selectivity in a mixed metal solution (Scheme 2).[9]

To overcome this fundamental limitation, special monomers with high selectivity have been designed. For example, ammonium molybdophosphate has long been known for its high selectivity for cesium sorption.[10–14] A series of calixcrowns also show high selectivity for certain metal ions such as cesium and strontium.[15–18] However, commercialization of these new monomers has been hampered by high costs and poor solubility. For these reasons, modification of one existing functional group would be a very rewarding trial, and crosslinking of the graft chains might be a possible strategy.[19,20] Saito demonstrated that crosslinking was a countermeasure to the drawback of expansion of the charged graft chains which depend on the ionic strength, pH value, and type of solvent used.[21,22] An appropriate degree of crosslinking of the graft chains is effective in reducing the swelling and accordingly improved permeation flux.[20,23,24] This implied that graft chains were tightened by crosslinking. The crosslinking agents of divinylbenzene and triallyl isocyanurate were also used to improve the crosslinking network and pure water flux.[19,20,24,25] Hence, early signs demonstrated that crosslinking would also change the sorption behavior of an adsorbent to a certain extent.
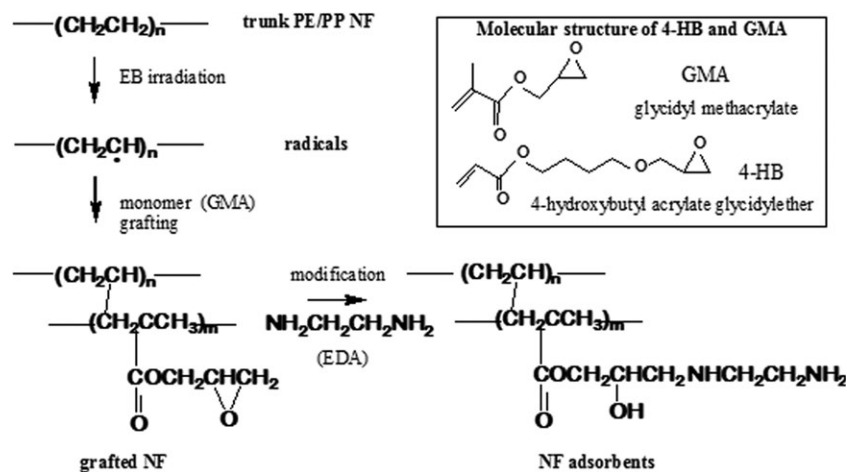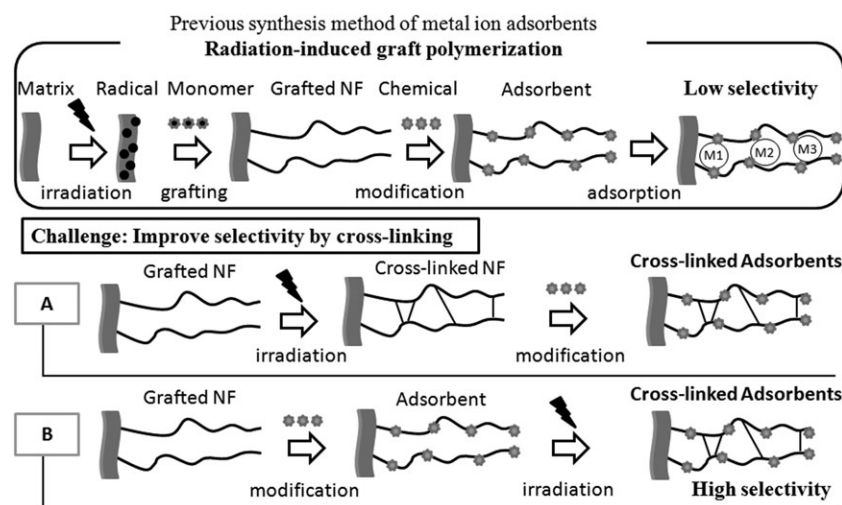
Scheme 1. Preparation scheme of amine-type (EDA) adsorbents. Inset: Molecular structure of 4-HB and GMA.

Glycidyl methacrylate (GMA) is a widely used precursor monomer for graft polymerization as the epoxy group can be easily modified into functional groups in a ring-opening reaction.[26–28] Radiation-induced graft polymerization of GMA can be performed at a low adsorbed dose in both organic solvent and water emulsion.[29–31] To date, GMA has been successfully grafted onto all kinds of matrix polymer such as PE, PP, polyvinylidene difluoride, and others. In our previous article, we reported the graft polymerization of a new monomer 4-hydroxybutyl acrylate glycidylether (4-HB) which shares a similar chemical structure with GMA (Scheme 1) and found 4-HB-grafted adsorbent showed not only better mechanical property, but also a higher adsorption capacity.[32] The mechanism briefly illustrated that a subtle distinction of four methylene groups in 4-HB made some parts in the secondary side chain longer and more flexible (Scheme 3).[32] Considering the four methylene groups in the secondary side chain, crosslinking would be introduced into the polymer, especially into the side chain of the polymer. By this means, the distance of a functional group can be reduced and the selectivity of the adsorbent might change.

Methods for crosslinking include ionic crosslinking, radiation crosslinking, and cografting of crosslinkers with precursor monomers.[19] Intensive investigations have concentrated on radiation-induced crosslinking of polymer to enhance their mechanical and thermodynamic properties such as in crosslinked PE-insulated cable, fuel cell membranes, and so on.[33–36] In this article, we propose a novel method for crosslinking. Radiation-induced crosslinking of the amine-type adsorbent was performed in water to improve selectivity. No crosslinker was used and an optimal approach for crosslinking was given. Investigations on the properties of the material were carried out by means of gel fraction, water content, and an examination of the selectivity of metal ions. The results show that a crosslinked amine-type adsorbent can select Cu^{2+} from a Cu^{2+}/Pb^{2+} mixed solution. A desirable selecting performance and mechanism are demonstrated, which could provide new ideas for the preparation of high-selectivity adsorbents.

Scheme 2. Preparation scheme of crosslinked amine-type adsorbents. Inset: Previous synthesis method of metal ion adsorbents.
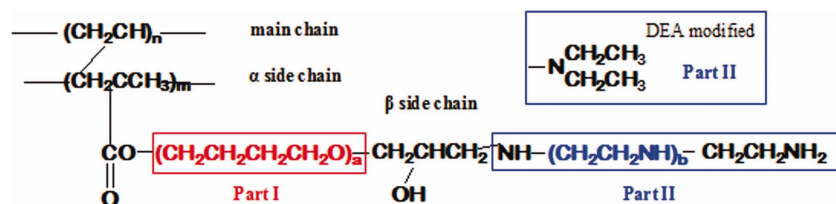
Scheme 3. Molecular chains of the amine-type adsorbents. Inset: DEA-type adsorbent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

EXPERIMENTAL

Materials

Polyethylene-coated polypropylene (PE/PP) nonwoven fabric (NF) obtained from Kurashiki MFG was used as the trunk polymer. A monomer of 4-HB and GMA was purchased from Tokyo Kasei Kogyo, Japan, and used without further purification. Ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), diethylamine (DEA), surfactant sorbitan monolaurate (Span-20), xylene, and isopropyl alcohol (IPA), copper and lead standard solution for quantitative analysis (1000 ppm), copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), copper dichloride hydrate ($CuCl_2 \cdot 2H_2O$), copper oxalate, copper acetate, and copper citrate, and ultrapure nitric acid (ultrapure-100) were purchased from Kanto Chemical. Potassium hydroxide was 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.

Synthesis of Noncrosslinked Adsorbent

Adsorbents were prepared based on radiation-induced polymerization (Schemes 1 and 2). NFs of 3 cm × 7 cm square pieces were packed into PE bags. After the substitution of air in the PE bag with nitrogen gas, the NF pieces were cooled at dry-ice temperature and irradiated at a dose of 30 kGy by an electron beam (EB) accelerator with energy of 1.5 MeV and beam current of 2 mA. The irradiated NF pieces were transferred to a glass ampoule and the air inside was evacuated under reduced pressure. Then, an aqueous emulsion containing 5% monomer and 0.5% Span-20 was drawn into the glass ampoule via suction.[32–38] Graft polymerization of 4-HB and GMA was carried out, respectively, by keeping the glass ampoule at 40°C in a water bath. After 2 h, 4-HB was grafted into the trunk polymer at a degree of grafting (D_g) of 135%. In the case of GMA, after 45 min, GMA was grafted into the trunk polymer at a D_g of 100%.

4-HB-grafted and GMA-grafted NFs were modified by a variety of amine-type compounds. In the case of EDA, DETA, and TETA, grafted NFs were reacted with 70% of EDA, DETA, and TETA in IPA at 60°C for 4 h, respectively. DEA modification was performed in 50% DEA/water solution at 30°C for 6 h.[32,33] After modification, the adsorbents were removed from the solution, washed three times with distilled water, and dried under reduced pressure. The density of the amine group of the adsorbents was estimated as described previously.[32]

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

where Z_0 and Z_i are the weights of grafted NF before and after chemical modification and M the molecular weight of the amine compound.

Crosslinking Process

The samples were sealed in a PE bag with water, and then irradiated at a specific dose by the same EB accelerator described in **Synthesis of Noncrosslinked Adsorbent** section. Two crosslinking approaches were investigated: crosslinking done before chemical modification, but after grafting [Scheme 2(A)]; and crosslinking done after chemical modification [Scheme 2(B)].

Gel fraction of the polymer before and after crosslinking was determined after the sample was extracted in boiling xylene for 8 h. Water content was determined as follows: NFs were soaked in pure water for 24 h at room temperature. A series of wet weights varying with time were measured after carefully wiping up the NF surface and the true value of water-containing adsorbent (W_a) was obtained from an extrapolation. The dry weight of the adsorbent (W_b) was obtained by drying the samples at 30°C for 24 h under reduced pressure. The water content was defined as follows:

$$W(\%) = (W_a - W_b)/W_b \times 100 (\text{gH}_2\text{O}/\text{gdryNF})$$

Adsorption and Elution, Column, and Batch Mode

The prepared adsorbents were cut into pieces with a diameter of 7 mm and then packed in a column. Column adsorption and elution were carried out using a PSM071AA model peristaltic pump and a CHF122SC model programmable fraction collector, the details of which are described elsewhere.[39] Individual or mixed feeding solutions with 10 ppm metal ions at pH 5 were pumped through the column at a designated flow rate. Effluent samples for analysis were collected at required time intervals using the fraction collector. The concentrations of the metal ions were measured using an optical emission spectrometer (Optima 4300 DV). The breakthrough point was defined as feeding volumes at the concentration ratio of feeding solution to effluent solution (C/C_0) up to 0.05, where C_0 and C represent concentrations of metal ion in the feeding solution and in the column effluent, respectively. After C/C_0 reached a saturate value, $1M$ hydrochloric acid solution was used to carry out the elution test.

For batch adsorption tests, amine-type adsorbents of 0.02 g were soaked in 45 mL metal ion solutions with an initial concentration of 10 ppm at pH 5. The removal ratio (R) of metal ions was evaluated as follows:

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

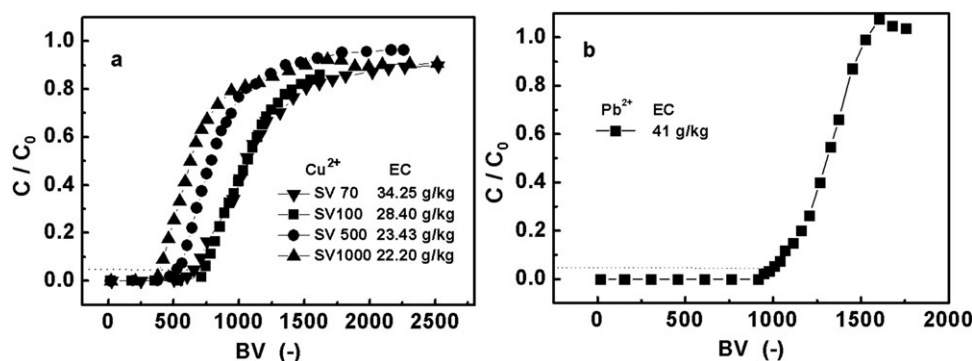where C_0 and C_i are the concentrations of the metal ions in solution before and after adsorption.

Figure 1. Breakthrough profiles of Cu^{2+} (a) and Pb^{2+} (b) from a column packed with EDA-type adsorbent.

RESULTS AND DISCUSSION

Adsorption Capacity of the Noncrosslinked Adsorbent

EDA-type adsorbent was prepared based on our previous study (Scheme 1).[32] The adsorption capacity of the adsorbent was evaluated in the column mode. Figure 1(a) shows the typical breakthrough curves of Cu^{2+} solutions. The abscissa is the bed volume (BV) defined as the volume ration of the effluent and the absorbent. The ordinate is the relative metal ion concentration of the effluent to the feed. The breakthrough curves were observed by pumping 10 ppm Cu^{2+} solution into the EDA-type column with different flow rates in a range from 70 to 1000 h^{-1} in space velocity (SV). The curves are essentially independent of relatively lower flow rates below 100 h^{-1} SV and the breakthrough points were 740 BV as shown in Figure 1(a). From the area of the breakthrough curve, the equilibrium adsorption capacity (EC) was evaluated as 34 g/kg of the adsorbent. At higher SV the breakthrough curves left shifted slightly as diffusional mass-transfer resistance of metal ion to the amino group is not negligible. EC was evaluated as 22 g/kg at an extremely high flow rate of 1000 h^{-1} SV which is 130 times faster than that of a normal granular resin-packed column.[26,40]

EDA-type adsorbent also shows very rapid removal of Pb^{2+} from its water solution. Breakthrough curves were observed with a flow rate of 100 h^{-1} SV by pumping 10 ppm Pb^{2+} solution into the column. The breakthrough point was observed at 1000 BV as shown in Figure 1(b). EC was evaluated as 41 g/kg of the adsorbent. After adsorption, both Cu^{2+} and Pb^{2+} can be very easily eluted by $1M$ hydrochloric acid. The adsorbed Cu^{2+} and Pb^{2+} ions were almost completely eluted after 20 BV at a flow rate of 100 h^{-1} SV.

Similarly, the adsorption capacity of these 4-HB grafted EDA-type adsorbents was investigated by using a mixed solution containing 10 ppm Cu^{2+} and 10 ppm Pb^{2+}. Breakthrough curves were observed with a flow rate of 100 h^{-1} in SV. The breakthrough points of Cu^{2+} and Pb^{2+} were observed at 520 and 480 BV, respectively, as shown in Figure 2. Compared with the results from their individual solution, the breakthrough points of both metal ions left shifted as a matter of course, whereas the value from Pb^{2+} decreased more remarkably. The EC of this EDA-type adsorbent was evaluated as 28 g/kg of Cu^{2+} and 19 g/kg of Pb^{2+}, respectively, which means it still cannot be used in the separation of a Cu^{2+} and Pb^{2+} mixed solution.

The mechanism of the adsorption and separation of heavy metal ions is a research field of continued interest. As mentioned in **INTRODUCTION** section, intrinsic adsorbability is determined by a combination of various factors. Generally, one type of adsorbent shows low selectivity when used in mixed metal ion solutions. From our above results, it is apparent that when this EDA-type adsorbent was used in a Cu^{2+}- and Pb^{2+}-mixed solution, both of the metal ions are adsorbed and there is little of evidence that they can be separated.

Crosslinking Process of the Polymer

Irradiation, especially direct exposure to a high-energy irradiation source is widely used to crosslink polymeric materials.[35–38,41] However, the results show that this is not the most effective method. PE/PP NF was irradiated under EB by two means: one in a dry condition and another in a wet condition. Gel fractions of PE/PP NFs increased with irradiation dose in both conditions (Figure 3). Dry NF achieved a 15% increment of gel fraction after 500 kGy irradiation, whereas PE/PP NF immersed in water obtained a 40% increment of gel fraction. Higher gel fraction stands for higher degree of crosslinking,[42] which means the wet condition shows merit in the process of crosslinking. As widely known, the hydrogen abstraction reaction is the key factor in the crosslinking process. In the
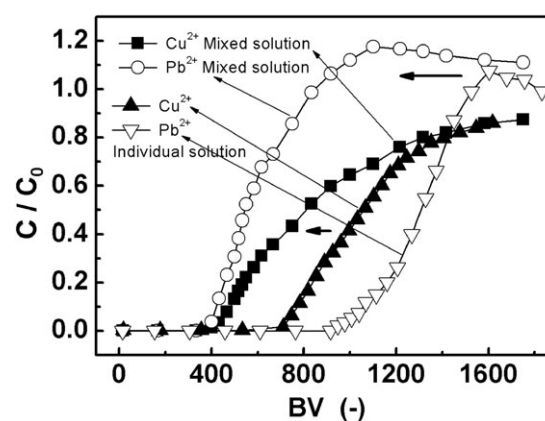

Figure 2. Breakthrough profiles of Cu^{2+} and Pb^{2+} from a column packed with EDA-type adsorbent. (■) Cu^{2+} from the mixed solution, (▲) Cu^{2+} from its individual solution, (○) Pb^{2+} from the mixed solution, and (▽) Pb^{2+} from its individual solution.
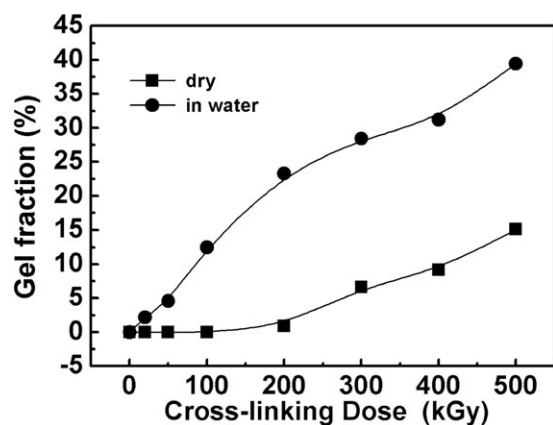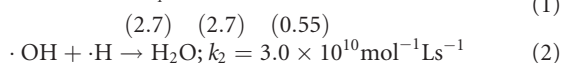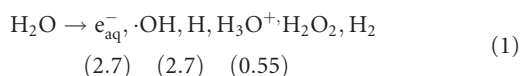
Figure 3. Gel fraction of PE/PP NF before and after irradiation in dry condition and water condition.

Figure 4. Gel fraction of grafted and modified PE/PP NFs before and after crosslinking.

irradiation system of the wet condition, two phases were involved: water and polymer. It is well known that a series of primary active species are generated from the radiolysis of water (eq. (1)). Values in parentheses are the radiation chemical yields of these species at pH 7.0, viz., G-values, which are defined as the number of formed or decomposed molecules per 100 eV of absorbed energy.[43] Because of the high G-value and high-reaction rate constant of the hydrogen abstraction reaction (eq. (2)), the most reactive radical of hydroxyl (OH) plays a dominant role in the process of the hydrogen abstraction reaction in a water solution.[43] In the case of the polymer used here, a series of primary alkyl radicals are formed under irradiation.[44–46] In view of the mobility of radicals, the long-range migration of radicals during and after irradiation, the hydrogen abstraction reaction between ·OH and H released from the polymer is quite considerable and efficient.[44–46] Accordingly, the recombination among alkyl radicals should be more efficient. Hence, crosslinking will be more facile in water than that in the dry state.

$$H_2O \rightarrow e^-_{aq}, \cdot OH, H, H_3O^+, H_2O_2, H_2 \qquad (1)$$
$$(2.7) \quad (2.7) \quad (0.55)$$
$$\cdot OH + \cdot H \rightarrow H_2O; k_2 = 3.0 \times 10^{10} mol^{-1}Ls^{-1} \qquad (2)$$

Preparation of Crosslinked Adsorbent
Based on the above result, all crosslinking processes in this article were carried out in water. The irradiation gel fraction shown in Figure 4, indicating that crosslinking was achieved from both the A and B approaches shown in Scheme 2. Following Scheme 2(B), the obtained normal EDA-type adsorbent was irradiated at different irradiation doses in a range of 20–500 kGy to bring about crosslinking. The gel fraction before and after irradiation is shown in Figure 4. Before irradiation, the gel fraction of the initial EDA-type adsorbent is 67%, which is owing to the grafting of 4-HB onto a trunk polymer. The gel content increased steadily up to 77% at a dose of 500 kGy. The higher the gel content, the higher the degree of crosslinking in amorphous regions. A 10% increment of gel fraction implies crosslinking occurred in the polymer. In the case of grafted-only material [Scheme 2(A)], crosslinking was carried out before modification. Figure 4 shows that the increment of gel fraction was even
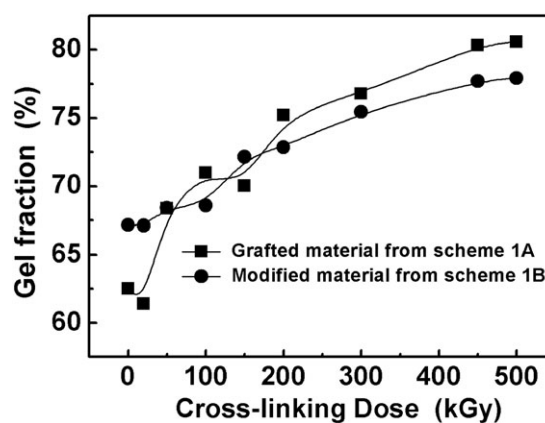
a little higher (18%) than the modified material obtained from Scheme 2(B). Generally, a 10% increment is sufficient evidence for crosslinking.[37,42] However, based on our further research, adsorbent prepared from Scheme 2(A) did not show any improvement in selectivity. For reasons of space constraints, we omit a detailed explanation in this article and all the results and discussion below are from Scheme 2(B).

Meanwhile, the water content of the modified material obtained from Scheme 2(B) also confirmed the effects of crosslinking. The water content rapidly reduced with dose increments until 150 kGy and then the extent slowed down with further increase of the dose (Figure 5). The lower water content also implies a higher degree of crosslinking.

The scanning electron microscopy (SEM) images of the surface sections from the EDA-type adsorbent before and after crosslinking are shown in Figure 6. The surface section image of the fabric reveals the fiber morphology, crisscrossed by a network of fibers that were 20 μm in diameter. From our previous research, there is no evidence of any destruction happening to the material after modification with EDA [Figure 6(a)].[31] After the second-round irradiation, the material shrank slightly after 50 kGy irradiation [Figure 6(b)]. Meanwhile, after a high-dose
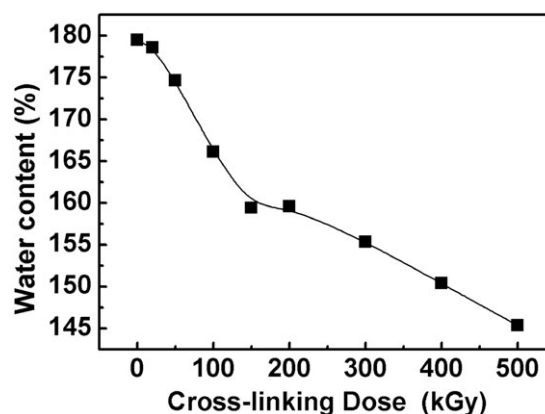

Figure 5. Water content of EDA-modified PE/PP NFs before and after crosslinking.
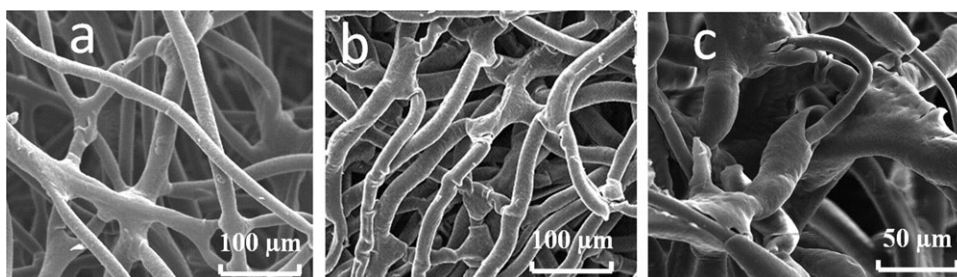
Figure 6. SEM images from the surface of EDA-modified NFs before and after crosslinking: 0 kGy irradiation (a), 50 kGy irradiation (b), and 500 kGy irradiation (c).

irradiation of 500 kGy, the deep extent of shrinkage led to some rupture in the outer layer of the material [Figure 6(c)]. SEM analysis of the morphology revealed the crosslinking from another point of view.

Improvement of Selectivity

Following Scheme 2(B), the obtained EDA-type adsorbent was made crosslinked under irradiation at different doses in the range of 100–500 kGy. Together with the uncrosslinked adsorbent, their adsorption capacities were investigated in column mode with a Cu^{2+}- and Pb^{2+}-mixed solution. The change of Cu^{2+} and Pb^{2+} concentration of the effluent with effluent volume is shown in Figure 7. Results revealed that the selectivity changed: the breakthrough curve of Cu^{2+} right shifted [Figure 7(a)] and the breakthrough curve of Pb^{2+} left shifted [Figure 7(b)]. The gel fraction of the EDA-type adsorbent before and after crosslinking in Figure 4 gives a clue that 300 kGy irradiation resulted in a 7% increment of gel fraction, which means the degree of crosslinking is relatively low. However, Figure 7 shows that even a low degree of crosslinking resulted in a favorable breakthrough curve for the practical separation of Cu^{2+} and Pb^{2+}: the breakthrough curve of Cu^{2+} right shifted until 300 kGy irradiation, indicating the higher adsorption capacity of Cu^{2+} [Figure 7(a)], the breakthrough curve of Pb^{2+} left shifted until 500 kGy irradiation, indicating the lower adsorption capacity of Pb^{2+} [Figure 7(b)]. Meanwhile, it should be noted that after 600 BV, the Pb^{2+} concentration of the effluent greatly exceeded the initial feed solution ($C/C_0 > 1$), which means that the adsorbed Pb^{2+} ions were eluted by the feeding solution itself. After the adsorbent was made crosslinked, the Pb^{2+} ions were more easily eluted.

After calculating the area from the breakthrough curve, the EC of various degrees of crosslinked adsorbents is shown in Figure 8. Compared with the noncrosslinked adsorbent, EC of Cu^{2+} increased slightly, whereas that of Pb^{2+} decreased remarkably with increments of crosslinking dose. The maximum EC of Cu^{2+} was obtained from the adsorbent under 300 kGy irradiation as 40 mg/g-ad, which was 50% higher than the value from the noncrosslinked adsorbent. Meanwhile, Pb^{2+} was rapidly eluted by the feeding solution. The EC of Pb^{2+} was almost 0 from the adsorbent under 300 kGy irradiation, which means the crosslinked adsorbent can adsorb only Cu^{2+} in the mixed solution. High selectivity between Cu^{2+} and Pb^{2+} was eventually achieved by the means of crosslinking. Further irradiation at a higher dose of 500 kGy and 1 MGy resulted in a decrease of EC of Cu^{2+}, which indicates that the 300-kGy dose would be adequate to improve selectivity between Cu^{2+} and Pb^{2+}.

The above results were obtained in a Cu^{2+} and Pb^{2+} nitrate solution. The sulfate and chloride of copper were used and a similar result was obtained from the batch mode adsorption test. Meanwhile, a similar phenomenon was obtained when the crosslinked adsorbent was used in organic salts of copper oxalate, copper acetate, and copper citrate, which indicates that selectivity between Cu^{2+} and Pb^{2+} is independent of the anions in solution.

The above results indicated that crosslinking improved the selectivity of the material. This might be owing to the change in distance of the chelating group. The radius of a single Pb^{2+} ion is much larger (0.120 nm) than Cu^{2+} (0.072 nm). Once the distance of the chelating group was reduced by crosslinking, it
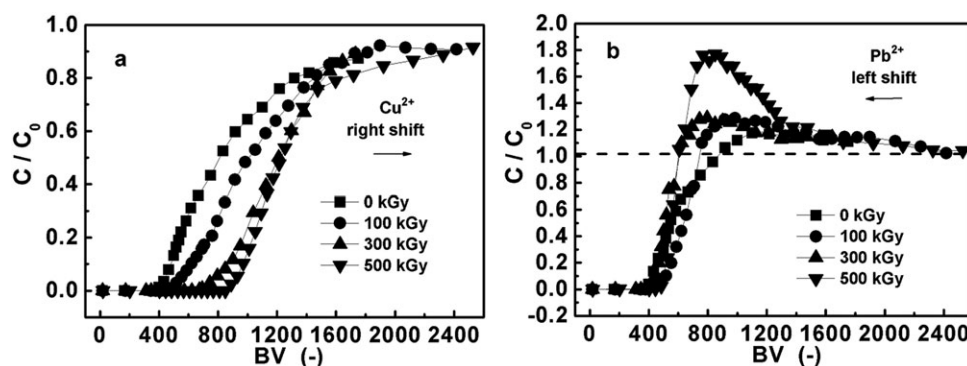

Figure 7. Breakthrough profiles of Cu^{2+} (a) and Pb^{2+} (b) from their mixed solutions, from a column packed with crosslinked EDA-type adsorbents of various degrees.
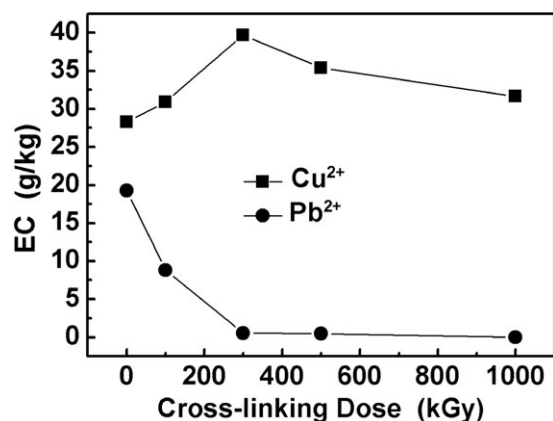
Figure 8. Equilibrium adsorption capacities of Cu^{2+} and Pb^{2+} from crosslinked EDA-type adsorbents of various degrees.

would be more efficient for the amino functional groups to catch the relatively smaller Cu^{2+} ion. To explain the structure of a polymer, the definition of a main chain and side chain are very well covered in the literature and are schematically shown in Scheme 3. For our particular adsorbent, the functional group is located on the secondary side chain (β-side chain). With irradiation, crosslinking occurred in the main chain, α-side chain, β-side chain, and each other simultaneously. Although the increase of gel fraction stands for the degree of crosslinking, the data in this region were not very accurate and no attempt was made to calculate the proportion of crosslinking that happened and in which part of the polymer.

Although we cannot distinguish which part of the polymer was involved in the crosslinking clearly, it would be worthwhile to study the length effect from some parts of the β-side chain. Apart from 4-HB, a GMA-type adsorbent was also synthesized and modified by EDA with the same conditions. The results from the batch adsorption test of the Cu^{2+}- and Pb^{2+}-mixed solution are summarized in Table I. First, it should be stated that it takes a long time to reach the adsorption equilibrium (3 days). Second, the improvement of selectivity was less extraordinary than that from the 4-HB-type adsorbent. After being crosslinked, the GMA-type adsorbent gave birth only to a 40% dif-

ference value ($R(N) - R(C)$, Table I), which is 27% lower than that of the best 4-HB-type adsorbent. As mentioned above, the 4-HB-type adsorbent has a longer **Part I** in the β-side chain compared with the GMA type (Schemes 1 and 3). The longer and more flexible **Part I** shows merit for improving the selectivity of the material by the means of crosslinking as four methylene groups act as a radical and hydrogen donor. Methylene can be easily changed into alkyl radicals and H (Scheme 1) under irradiation. The flexible four methylene groups also improve the mobility of radicals, migration of radicals, and recombination of alkyl radicals that are more likely to react with another one in the adjacent β-side chain.

In addition to EDA, as a comparison DETA, TETA, and DEA were also used to modify 4-HB-grafted material. Aminated material was obtained correspondingly. Then DETA-, TETA-, and DEA-type adsorbents were also made crosslinked under 300 kGy irradiation and the results from a batch adsorption test of mixed Cu^{2+} and Pb^{2+} solution are summarized in Table I. Compared with the noncrosslinked adsorbents, the difference value of removal ratio from Cu^{2+} and Pb^{2+} decreased in the following order: EDA > DETA > TETA > DEA. The chemical structures of these ethylene amines indicate that long ethylene amines (**Part II**) show a less favorable effect for selectivity improvement by crosslinking. The reason might be that crosslinking more likely happened in **Part I** of the β-side chain rather than **Part II**. In the case of DEA, a possible steric hindrance effect from the two ethyl groups makes it more difficult and incapable of enhancing selectivity by crosslinking. Hence, the results at present show that a longer **Part I** and a shorter **Part II** in the β-side chain would be advantages to generating crosslinking by means of irradiation.

CONCLUSIONS

Amine-type adsorbents prepared by radiation-induced 4-HB graft polymerization showed good sorption behavior for Cu^{2+} and Pb^{2+} as individual metal ions, but low selectivity when mixed in solution. To increase the selectivity of the adsorbent, crosslinking induced by irradiation was initially proposed in this research. Several approaches for crosslinking were attempted and the optimum route was carried out in aqueous

Table I. Difference Value of Removal Ratio Between Cu^{2+} and Pb^{2+} from all Kinds of Adsorbents

Removal ratio (R) (%)		$R(Cu^{2+})/R(Pb^{2+})$	$R(Cu^{2+})-R(Pb^{2+})$		Difference value $R(N) - R(C)$
4-HB-EDA	Noncrosslinked (N)	97/94	$R(N)$	3	**67**
	Crosslinked (C)	98/18	$R(C)$	70	
4-HB-DETA	Noncrosslinked (N)	97/90	$R(N)$	7	**30**
	Crosslinked (C)	97/60	$R(C)$	37	
4-HB-TETA	Noncrosslinked (N)	93/87	$R(N)$	6	**20**
	Crosslinked (C)	96/70	$R(C)$	26	
4-HB-DEA	Noncrosslinked (N)	75/32	$R(N)$	43	**13**
	Crosslinked (C)	76/20	$R(C)$	56	
GMA-EDA (3D)	Noncrosslinked (N)	97/85	$R(N)$	12	**40**
	Crosslinked (C)	97/45	$R(C)$	52	

conditions after the polymeric matrix was grafted by 4-HB and modified by EDA. Evidence of 10% increment from gel fraction, 35% decrease of water content, and shrinkage of the material from the SEM analysis demonstrated that the adsorbent was crosslinked by means of irradiation in aqueous conditions. After 300-kGy irradiation, the crosslinked adsorbent exhibited a higher capacity for Cu^{2+} and almost no capacity for Pb^{2+} compared with the noncrosslinked version, which means that the selectivity was improved. The results in this research revealed crosslinking would be a feasible way to change the selectivity of an adsorbent. Studies of structure and mechanism would be of great significance and new techniques and methods would be used to estimate the distance of a functional group before and after crosslinking, which is expected in the near future.

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