

Synthesis, Characterization, and Application of Polyethersulfone Bound-Iminodiacetic Acid

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ABSTRACT: A new method to introduce iminodiacetic acid (IDA) onto polyethersulfone (PES) matrix through chlorosulfonation was described in this work, and the prepared PES-IDA was used as adsorbent for the removal of metal ions from aqueous solutions. Chlorosulfonic groups ($-\text{SO}_2\text{Cl}$) were introduced onto PES first, then IDA was grafted onto PES by using the interactions between the chlorosulfonic group and the imino group of IDA. The grafted IDA was characterized by fourier transform infrared measurement, X-ray photoelectron spectroscopy analy-

sis, and thermogravimetric analysis spectra. The adsorbed amounts by the PES-IDA for Cu^{2+} and Ag^+ were 3.44 mg/g and 7.09 mg/g, respectively. The PES-IDA adsorbent may expand the usage of PES in purification fields and could make some potential contributions to the polymer-based adsorbents. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 345–350, 2011

Key words: modification; polyethersulfone; chlorosulfonation; adsorption

INTRODUCTION

Polymer-adsorbent complexes are widely used in both laboratory and large scale applications, such as waste water treatment, water purification, catalyst system, and so on.^{1–3} Therefore, synthesis and application of polymer-based adsorbents have received considerable attentions in recent years.

The polymer-based ion-exchange resins show great dependence on functional groups, and grafting functional groups onto polymer matrix is the most widely used method. Among the chelators, ethylenediaminetetraacetic acid (EDTA) forms strong and stable complexes with a wide range of metal ions in a single step. However, it is difficult to introduce EDTA into polymer chains and the EDTA would also cause some other problems in waste water treatment.⁴ An organic chelator, iminodiacetic acid (IDA), which contains one reactive aminopolycarboxylate and two carboxyl groups for chelation, is widely used. IDA can be easily grafted to polymer chain, and the applica-

tions of IDA functionalized polymer had been reported in recent years.^{5,6} Because of the good metal-ion adsorption performance,⁷ polymer-IDA-metal complexes show widespread availability in various fields, such as separation of rare earth elements,⁸ catalyst system,⁹ protein separation,^{10,11} and so on.

To introduce IDA into polymer chain, the traditional method is to graft epoxides like epichlorohydrin¹² and glycidyl methacrylate^{3,13} to polymer main chain firstly, and then graft IDA molecules by opening the epoxy ring. In this method, epoxides are introduced mainly through radiation; however, it is inconvenient to control the grafting rates. Sometimes, it is difficult to introduce the epoxides through radiation, thus coating porous membranes with functional epoxy groups were used.^{14–18}

To avoid these shortcomings, a new method to introduce IDA into polymer chain through chlorosulfonic group was investigated in this study. Polyethersulfone (PES) was chlorosulfonated with chlorosulfonic acid (CSA) first, and then grafted with IDA through the chlorosulfonic group. The modified PES was prepared as particle adsorbent, and the adsorptive ability of the adsorbent was investigated by using Cu^{2+} and Ag^+ solution, respectively. PES shows outstanding thermal and hydrolytic stabilities, as well as good mechanical and film-forming properties. Therefore, it is reasonable to predict that by grafting IDA onto PES, useful and novel adsorbents may be obtained.

To our knowledge, the preparation of PES grafted with IDA and the PES-IDA adsorbents have not been yet reported. We anticipated that this new type

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of PES-IDA adsorbent may expand the usage of PES for purification, and this novel method of introducing IDA onto polymers through chlorosulfonation could make some contributions to the adsorption fields.

EXPERIMENTAL

Reagents

PES (Ultrason E6020P, CAS Number: 25608-63-3) was obtained from BASF (Beijing, China), and dried in an oven at 100°C for 2 h before use. CSA (Chemical Pure), dichloromethane, copper (II) sulfate pentahydrate (CuSO_4), silver nitrate (AgNO_3), and sodium hydroxide (NaOH) were obtained from Kelong Chemical Company (Chengdu, China). IDA was provided by Sinopharm Chemical Reagent (Shanghai, China). Ethylene diamine tetraacetic acid disodium salt (EDTA-2Na) was purchased from Kermel Chemical, (Tianjin, China). All the other chemicals are of AR grade and used as received.

Synthesis of PES-IDA

The procedure for the preparation of PES-IDA was shown in Figure 1. The chlorosulfonated PES (CSPES) samples were prepared according to the following steps. Five grams of PES was added to 25 mL methylene chloride, followed by dropping 25 g CSA (dissolved in 20 mL methylene chloride) into the solution while stirring at room temperature. This process was carried out under nitrogen atmosphere. After a determined reaction time, the reaction product was slowly moved into ice-cold deionized water and was washed until the pH was $\sim 6-7$.¹⁸

Five grams of the CSPES obtained earlier was dissolved in 5 g dimethylacetamide, followed by adding 11 g (Na_1IDA)-water (1/10, w/w) mixture. The reaction was carried out under nitrogen atmosphere at room temperature for 5 h. After that, the mixture was dried in a vacuum oven at 50°C to remove the redundant solvent and then washed with deionized water to remove the unreacted IDA.

Characterization and determination of CSPES

The fourier transform infrared measurement (FTIR) spectra of PES and CSPES were recorded using a Nicolet 560 spectrometer at the wavenumber of 600-4000 cm^{-1} . The $^1\text{H-NMR}$ (NMR-400, Bruker) spectrum was used to detect the occurrence of the chlorosulfonated groups. Deuterated dimethyl sulfoxide (d_6 -DMSO) was used to dissolve the polymer, and tetramethylsilane was used as the internal standard.

The degree of chlorosulfonation (DC) was measured by titrating based on ion-exchange method.¹⁹ First, 0.2 g CSPES was dissolved in 20 mL NaOH solution (2 mol/L) at 100°C while stirring for 1 h.

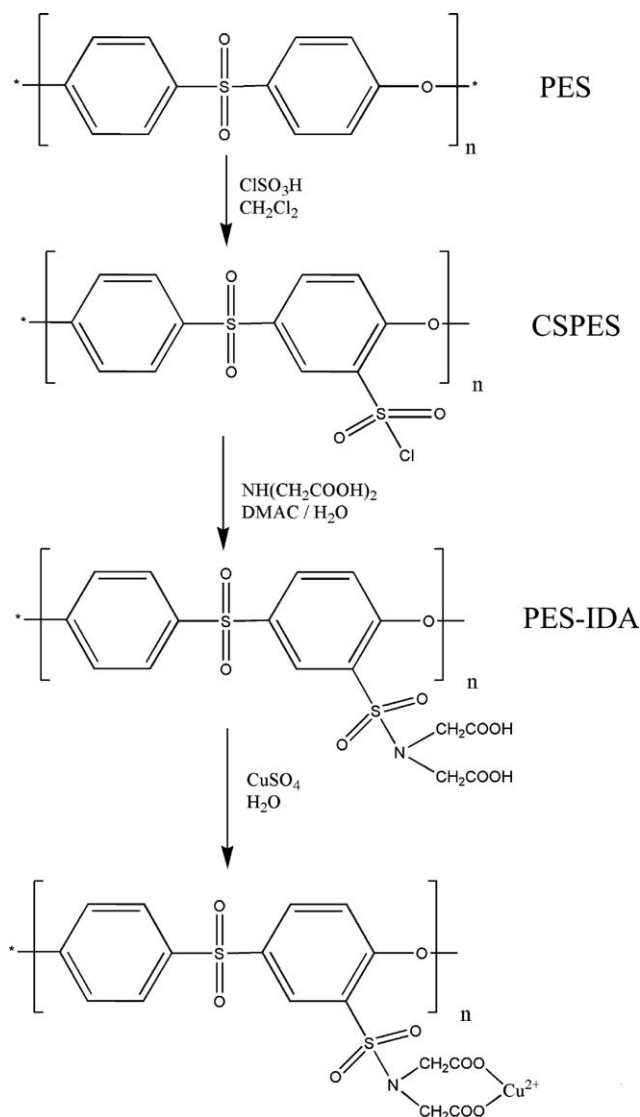


Figure 1 Schematic diagram for grafting IDA into PES.

Then, 10 mL clarifying solution of the mixture was taken and the pH was adjusted to 7-7.15. At last, standard AgNO_3 (0.01 mol/L) was used to titrate the solution from grass green to brick red using 0.5 mL 5% K_2CrO_4 as indicator. The following equation was used to calculate the DC:

$$\text{DC} = \frac{0.232M(\text{AgNO}_3) \times V(\text{AgNO}_3)/W - 0.129M(\text{AgNO}_3) \times V(\text{AgNO}_3) \times 100\%}{W}$$

Characterization of PES-IDA

X-ray photoelectron spectroscopy (XPS) analysis of the PES-IDA was performed using a KRATOS XSAM800 instrument. Survey spectra were run in the binding energy range 0-1000 eV and the high-resolution spectra of N1s were collected. The thermogravimetric analysis (TGA) spectra of PES, CSPES, and PES-IDA were obtained on Micro-thermal

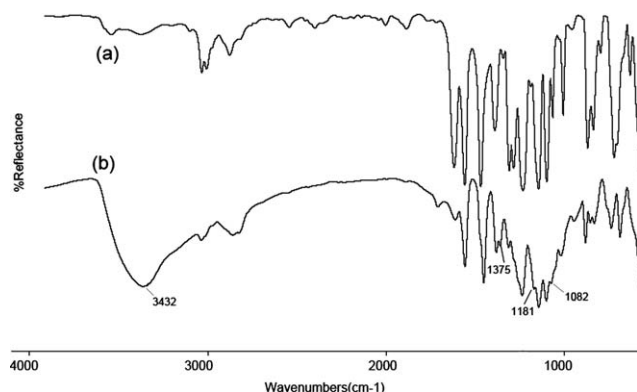


Figure 2 FTIR of (a) PES and (b) CSPES.

balance WRT-2P analyzer, from 50 to 800°C, heated at 10°C/min and at nitrogen atmosphere. Elemental analysis was performed using a CARLO ERBA 1106 elemental analyzer (Italy), with a carrier gas (He, at a flow rate of 100 mlmin⁻¹) at a combustion temperature of 1000°C.

Adsorption procedure

PES, CSPES/PES (1/5, m/m), and PES-IDA/PES (1/5, m/m) particles were prepared by using a liquid-liquid phase separation method.²⁰ For the adsorption experiment, ~ 0.1 g PES-IDA/PES particles were incubated in 20 mL 0.1 mM CuSO₄ solution for 12 h. And then, the particles were washed with deionized water to clear up the free Cu²⁺, and the particles were put into 20 mL 0.1 mol/L ethylene diaminetetraacetic acid sodium salt (Na₂EDTA) solution to remove the Cu²⁺ from the particles. The Cu²⁺ concentration in the elution was detected using an atomic absorption spectrophotometer (Model AA220Fs, Varian, Palo Alto, California). The Cu²⁺ adsorption for PES and CSPES/PES (1/5, m/m) particles were also investigated for comparison. The same procedure was also carried out for the adsorption of Ag⁺ using AgNO₃ solution.

RESULTS AND DISCUSSION

Chlorosulfonation of PES

Because the electron-withdrawing action of the sulfone groups (–SO₂–), the hydrogen on the benzene ring of PES became inactive. Thus, only the electrophilic reagent could react with PES. According to previous researches, three sulfonating agents, including SO₃,²¹ oleum,²² and ClSO₃H,²³ could be used for the modification of PES. Compared with SO₃ and oleum, when ClSO₃H was used in the sulfonation reaction, not only the sulfonic groups (–SO₃H) but also the chlorosulfonic groups (–SO₂Cl) would be grafted onto the polymer main chain.²⁴ However,

most of the previous researches only focused on the presence of sulfonic acid groups (–SO₃H) in PES and paid little attention to the chlorosulfonic groups (–SO₂Cl).^{25,26} Chlorosulfonic groups, which is more reactive than sulfonic group when reacting with an amino group at room temperature has been widely used as intermediate in organic synthesis. Hence, ClSO₃H was chosen as the sulfonating agent in this work, due to the simplicity and possibility of introducing chlorosulfonic groups.

To confirm the chlorosulfonation of PES, FTIR and ¹H-NMR were carried out. Figure 2 shows the FTIR spectra of PES and CSPES. The adsorption peak at 1181 cm⁻¹ in Figure 2(b) belongs to the SO₂ symmetric stretching vibrations of the chlorosulfonic group (–SO₂Cl), and the peak at 1375 cm⁻¹ belongs to (–SO₂Cl) symmetric stretching vibration.²⁷ These absorption peaks indicated that the PES was chlorosulfonated successfully and was grafted with the chlorosulfonic groups (–SO₂Cl). In addition, it could be seen that a characteristic sulfonic acid absorption peak at 1082 cm⁻¹ appeared in Figure 2(b). This could be attributed to the aromatic sulfonic group (–SO₃H) symmetric stretching vibrations, consistent with the literatures.^{25,28} The peak at 3432 cm⁻¹ was the characteristic of the stretching of the sulfonic group hydroxyl.

To determine the chlorosulfonation site, PES and CSPES were also characterized by ¹H-NMR spectroscopy. As shown in Figure 3, there was a significant down-field shift from 8.0 to 8.3 ppm; this was

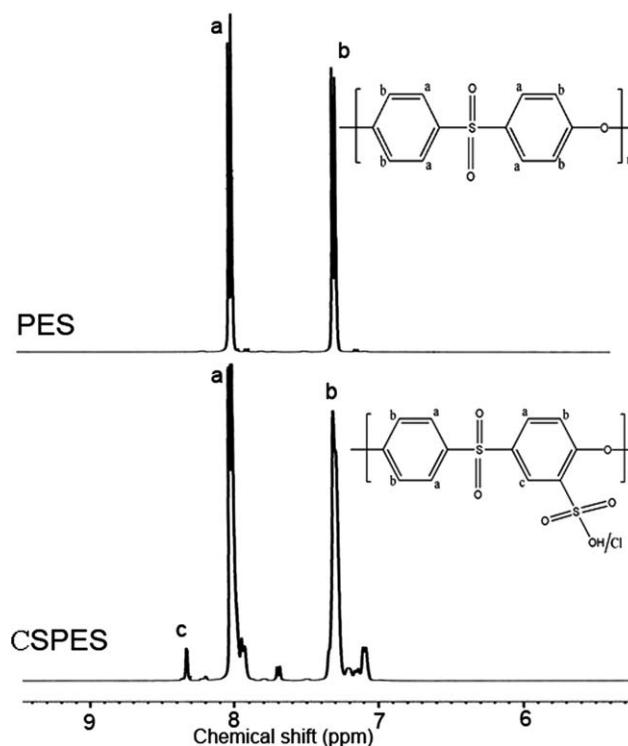


Figure 3 ¹H-NMR spectra of PES and CSPES.

TABLE I
Determination of DC and DS on the Reaction Conditions

PES/CSA (n)	Reaction time (h)	DC (%)	DS (%)
1/10	3	5.53	12.59
1/10	4	13.8	12.7
1/10	5	17.59	20.47
1/10	6	44.44	39.94
1/1	3	–	5.15
1/2	3	3.77	4.7
1/5	3	5.30	7.12

caused by the chlorosulfonic groups bonded to the benzene rings which affected the chemical shifts of the neighbor hydrogen atom located in the σ -position at the aromatic ring.^{28,29} The results also confirmed the successful introduction of chlorosulfonic groups onto PES.

The DC was the amount of the chlorosulfonic groups ($-\text{SO}_2\text{Cl}$) introduced onto PES. Besides, DC could influence the hydrophilicity of the material,²⁵ which was important in developing a new membrane for metal absorption.¹⁷ In this study, a series of CSPES samples with different times and different reactant ratios had been prepared. As shown in Table I, it can be seen that the DC increased with time and increased with the increase of the CSA amount. In addition, the hydrophilicity of the CSPES increased with the DC, as for some sample, the DC was too high that the CSPES was dissolved in water. The DC of the CSPES used for IR, TGA, and absorption measurement was 13.8%.

As mentioned earlier, there were not only chlorosulfonic groups ($-\text{SO}_2\text{Cl}$) introduced into PES, but also sulfonated groups ($-\text{SO}_3\text{H}$). DS was defined as the amounts of the introduced sulfuric acid ($-\text{SO}_3\text{H}$) groups, and could be calculated by nuclear magnetic resonance. As shown in Table I, at the reaction time

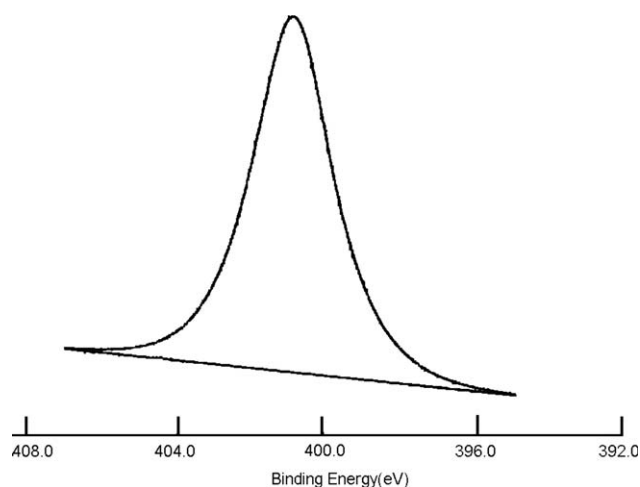


Figure 4 XPS of PES-IDA.

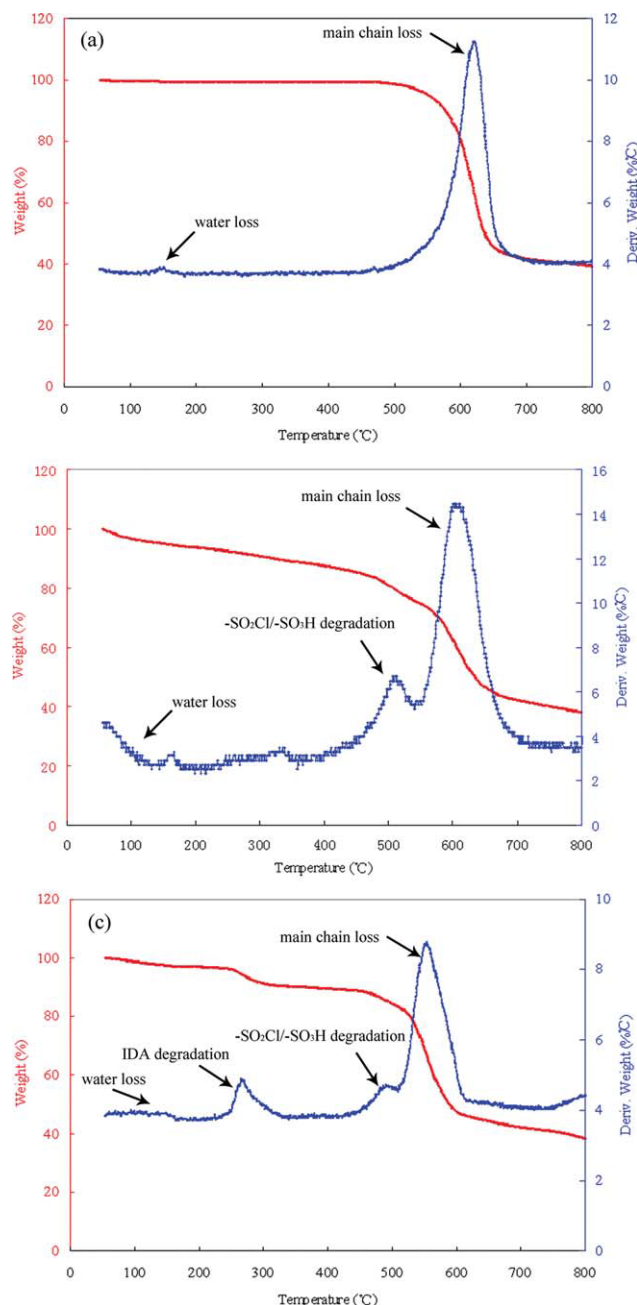


Figure 5 TGA thermograms of (a) PES, (b) CSPES and (c) PES-IDA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

over 4 h, the ratios of $\text{SO}_2\text{Cl} : \text{SO}_3\text{H}$ were approximately 1 : 1.

Grafting IDA

By using the interactions between the chlorosulfonic groups and imino groups, IDA was grafted onto PES. XPS was carried out to confirm the presence of the IDA in the PES chains. As shown in Figure 4, N1s peak appeared in the XPS spectra of PES-IDA. The N1s peak appeared in high binding energy area of

TABLE II
Elemental Analysis Data of PES-IDA

Sample	Carbon (%)	Hydrogen (%)	Nitrogen (%)
PES-IDA	56.01	3.22	0.66

~ 400.970 eV, compared with the standard N1s ~ 398.70 eV in the XPS of IDA,³⁰ which was caused by the strong attraction of the $-\text{SO}_2-$ of the benzene sulfonic amide in the modified PES chains. According to the characterization of XPS, the IDA had been introduced onto the CSPES.

The thermal stabilities of the PES, CSPES and PES-IDA were determined by TGA spectra, as shown in Figure 5. The parent PES was a thermostable polymer for which there was only one sharp weight loss at nearly 600°C, which could be ascribed to the decomposition of the PES polymer main chain. For the CSPES, as shown in Figure 5(b), the degradation was in three steps. First, ~ 5% weight loss around 100°C, which is related to desorption of water bonded to the sulfonic groups. Second, there was one gradually weight loss (~ 5%) at ~ 500°C, and this should be the stepwise degradation of the sulfonic acid groups from the polymer main chains. As for the third step, there was one sharp weight loss occurred at nearly 600°C which was in agreement with the main chain loss in PES. The TGA and DTG curve for the PES-IDA, as shown in Figure 5(c), was similar to that for the CSPES, except a small shoulder at around 250°C, which indicated the weight loss of IDA groups. Besides, it could be seen that after grafting IDA, the peak of $(-\text{SO}_3\text{H}-)$ and $(-\text{SO}_2\text{Cl}-)$ groups at 500°C became weaker than the same peak in the curve of CSPES, which indicated the weight loss of some $(-\text{SO}_2\text{Cl}-)$ groups with the IDA moiety together at 250°C.

To calculate the content of IDA introduced into the polymer, elemental analysis was used for PES-IDA; data are shown in Table II. Based on the elemental data of PES-IDA, it could be conclude that the content of IDA introduced in the polymer is ~ 13%, approach to the DC (13.8%), and the grafting rate of IDA reacting with sulfonyl chloride $(-\text{SO}_2\text{Cl})$ groups was ~ 90%.

TABLE III
Adsorption Ratio of Cu^{2+} by the Particles

Particles	Dry weight (g)	The absorption amount of Cu^{2+} (mg)	The absorption ratio (mg/g)
PES	0.1289	–	–
CSPES/PES (1/5, m/m)	0.1081	0.045	2.08
SPES-IDA/PES (1/5, m/m)	0.1016	0.070	3.44

TABLE IV
Adsorption Ratio of Ag^+ by the Particles

Particles	Dry weight (g)	The absorption amount of Ag^+ (mg)	The absorption ratio (mg/g)
PES	0.1022	–	–
CSPES/PES (1/5, m/m)	0.1013	0.068	4.03
SPES-IDA/PES (1/5, m/m)	0.1024	0.121	7.09

Adsorption of metal ions

To examine the adsorptive capacity of the prepared PES-IDA, the PES, CSPES/PES, and PES-IDA/PES particles were prepared, respectively. Different particles with different size have different surface area, and the particle size affect the adsorption amount. Thus, an appropriate and frequently used particle size^{31,32} (~ 1.6 mm) was chosen to detect the adsorptive capacity in this work. The adsorption of Cu^{2+} and Ag^+ by these particles was studied, as shown in Tables III and IV. As can be seen in Table III, for PES, there was no adsorption with Cu^{2+} , however, for the CSPES/PES and the PES-IDA/PES particles, the absorbed amounts were 2.08 and 3.44 mg/g, respectively. The adsorption of Cu^{2+} ions by the CSPES/PES particles was due to the effect of electrostatic crosslinking between the chlorosulfonic group and the positively charged ion of Cu^{2+} .¹⁸ Compared with the CSPES/PES particles, the PES-IDA/PES particles demonstrated an improved ability in adsorbing Cu^{2+} ions, and this increment was caused by the chelating agent of IDA grafted onto the PES. From the increment of the adsorbed Cu^{2+} of PES-IDA/PES, it could be presumed that the amount of the IDA grafted onto the PES through the chlorosulfuric acid was very high. The same conclusion can be found in Table IV.

The adsorbed metal ions could be removed by ethylene diamine tetraacetic acid (EDTA), and the adsorbent could be reused. Because the main aim of this work was focused on the modification of PES by grafting functional groups and the new method of grafting IDA, further study about the repeatability and reproducibility of the adsorbent will be considered in our following works.

CONCLUSIONS

In this study, a new adsorbent of PES-IDA was prepared through the chlorosulfonation of PES, followed by grafting IDA. The chlorosulfonated ratio increased with the reaction time and the amount of CSA used in the reaction. The IDA was grafted onto PES successfully through the chlorosulfonic groups. After grafting IDA, the metal ion adsorption

capacity increased, and the adsorbed amounts by the PES-IDA for Cu^{2+} and Ag^+ were 3.44 mg/g and 7.09 mg/g, respectively. We anticipated that this new type of PES-IDA adsorbent may expand the usage of PES for purification, and this novel method of introducing IDA onto polymers through sulfonation could make some potential contributions to the adsorption fields.

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