Study of Heavy Metal Ion Absorbance by Amidoxime Group Introduced to Cellulose-Graft-Polyacrylonitrile

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ABSTRACT: Amidoximated grafted cellulose was obtained by reacting hydroxylamine and cellulose-graft-polyacrylonitrile (C-g-PAN), prepared by $KMnO_4$/citric acid redox system, and the resultant amidoximated grafted cellulose was characterized by scanning electron microscope (SEM), solid-state NMR, FTIR, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and elemental analysis. The highest value of amidoxime content in the grafted sample was 2.42 mmol/g. The adsorption efficiencies of amidoximated grafted cellulose have been evaluated with studying different adsorption conditions. Amidoximated sample with amidoxime content 2.42 mmol/g showed high ability to adsorb the metal ions from the aqueous solutions as high as 1.7 mmol/g, 1.6 mmol/g, and 0.84 mmol/g for Co^{2+}, Cu^{2+}, Ni^{2+} ions, respectively, at the highest original metal ion concentration. These values are about three times larger than previous studies. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 866–873, 2011

Key words: cellulose; amidoximated grafted cellulose; heavy metals; adsorption behavior

INTRODUCTION

Heavy metal ion removal from water has been one of a big subject of technological research for environmental pollution control process.[1] Several different types of methods have been studied for the treatment of aqueous stream contaminated with heavy metal. Since the adsorption method of the toxic heavy metal ions may be the most effective and economic methods, different types of adsorbents such as polymers,[2–5] amorphous silica,[6–9] clays,[10–14] and zeolites[15–17] have been studied. Nevertheless, these materials yet have problems like low mechanical and thermal stability, poor removal efficiency, high cost, etc., so that development of new materials and modification of existing materials are still actively studied.

Concerning polymeric materials, those containing ionic and/or polar residues in main chain as well as in side chains have been tested. Cellulose is one of the promising candidates because it is the most abundant natural polymer which can be easily obtained and many derivatives can be prepared using hydroxyl residue. Cellulose derivatives called as chelating resins[18–22] have been reported that they have good adsorption properties for heavy metal ions. It is known that the chelating resins containing amidoxime groups[23–28] show selective adsorption for uranium from sea water. Those chelating resins are usually synthesized through the amidoximation of cyano groups in acrylic polymers grafted to cellulose by reacting with hydroxylamine. To improve both the stability against swelling of the resins and the free movement of the functional groups, samples prepared by different methods, that is, graft polymerization of acrylonitrile (AN) initiated by high-energy radiation,[29–31] Ce^{4+}, UV,[32] or photopolymerization,[33] are used for amidoximation with hydroxylamine and then adsorption efficiency of metal ions are examined. The maximum percent graft yield (GY), denoting percentage of increased weight of the sample after the graft copolymerization reached by above studies was in the range of 36-61% and amidoxime content (C_A), denoting the amount of nitrile group converted to amidoxime group after the amidoximation reaction was in the range of 1.6–2.1 mmol/g. The maximum adsorption of the metal ion (Cu^{2+}) by those samples was in the range of 0.5–0.7 mmol/g. In resent researches,[34] amidoximated bacterial cellulose was prepared and used to remove Cu^{2+} from aqueous solution where the maximum adsorption amount was 0.72 mmol/g. Mun et al.[35] prepared amidoximated *Pinus densiflora* bark from

polyacrylonitrile-grafted pink bark with GY of 70% and examined the metal ion adsorption, where the maximum adsorption amount of Cu^{2+} was 0.5 mmol/g. The maximum amount of Cu^{2+} metal ion adsorbed by amidoximated grafted sunflower stalk was 0.33 mmol/g.[36]

In a previous article,[37] we reported grafting of cellulose with AN using $KMnO_4$/citric acid redox system, in which GY reached as high as 70%. In this study, we use cellulose-graft-polyacrylonitrile (C-g-PAN) obtained by the above method for preparation of amidoximated resin and try to improve the adsorption efficiency. Factors affecting the formation of the amidoxime such as the reaction temperature and the reaction time are investigated. Samples thus obtained are characterized by scanning electron microscope (SEM), Fourier transform infrared (FTIR) spectroscopy, solid-state nuclear magnetic resonance (NMR), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). The amidoximated C-g-PAN was applied to recover the free metal ions such as Cu^{2+}, Ni^{2+}, and Co^{2+} from aqueous solutions. The adsorption efficiency of metal ions is examined at different conditions; amidoxime content, contact time, pH of the solution, metal ion concentration, and the nature of substrate used in the adsorption.

EXPERIMENTAL

Samples

C-g-PAN was prepared from Egyptian cotton cellulose samples (El-Mahalla Company for Spinning and Weaving, Egypt) and AN (Aldrich) using $KMnO_4$/citric acid redox system by the most efficient condition reported in a previous article.[37] Hydroxylamine, copper chloride, cobalt chloride, nickel chloride, methanol, and sodium hydroxide were received from Wako Pure Chemical Industries Ltd., Japan and used without further purification.

C-g-PAN (0.25 g) was allowed to react with 25 mL of 3.0 vol % hydroxyl amine solution in methanol : water = 1 : 1 mixed solvent at pH = 7.0 under reflux in oil bath at different temperatures and time. The resulting amidoximated C-g-PAN (AO-C-g-PAN) was separated and washed several times with methanol and dried at 50°C. The amount of the amidoxime groups introduced was estimated by the elemental analysis. The samples are distinguished by using percent GY and amidoxime content (C_A) such as C-g-PAN69 for sample with GY = 69.3% and AO2.42-C-g-PAN69 for the sample with C_A = 2.42 mmol/g.

Characterization

SEM micrographs of the untreated and the grafted cellulose fibers, coated with platinum by means of

Hitachi E-1030 ion sputter apparatus, were taken by Hitachi S-4100 SEM at an accelerating voltage of 10 KV. Elementa analysis was carried out by Perkin–Elmer 2400II CHN analyzer to determine C_A. Solid-state NMR measurements were performed by using Delta2-NMR spectrometer (B0 = 9.4T) with resonance frequency of 100.52 MHz. Zirconia rotors (6 mmϕ) with Aurum tube cape were used to hold samples. A 5-KHz spinning speed and decoupling with TPPM at $\gamma B1/2P$ = 100 kHz were used. For (CP)/MAS measurements, a 1H 90° pulse length of 5.25 μs and a contact time of 0.5 ms were applied. FTIR spectra were recorded with Bio-Rad FTS 6000 spectrometer with 32 scans at the highest resolution of 2 cm^{-1}. Approximately 1.0 mg of sample was pressed onto potassium bromide as a thin film with the thickness c.a.10 μm. Elemental analysis (C, H, and N) was performed by Perkin–Elmer 2400II CHN analyzer with acetanilide as a standard material. DSC measurements were performed using Seiko SDC-6220 with TAS100 controller in a temperature range of 25–450°C. The standard heating rate of 10°C/min was used under dry nitrogen atmosphere for sample mass of about 1.0 mg. TGA was carried out by a Seiko TG/DTA6300 in nitrogen atmosphere. The samples (1.1–1.4 mg) were heated from 20 to 600°C at a heating rate of 10°C/min.

Adsorption of the metal ions

Fifty milligram of the amidoximed grafted cellulose with different C_A were soaked into 50 mL of the buffered metal chloride solutions with different concentrations, whose pH was adjusted in a range of 2.0–5.5, at 30°C for different time (4–48 h) in a closed vessel for the adsorption test. The tested metal ions are Cu^{2+}, Ni^{2+}, and Co^{2+}. To determine the amount of metal ions adsorbed onto the amidoximated grafted cellulose, the metal ion concentrations remaining in the solution were determined by UV–Vis spectroscopy (Hitachi U-3200 spectophotometer).

RESULTS AND DISCUSSION

Characterization

To compare the difference in the physical appearance of untreated cellulose (Un-C), C-g-PAN and AO-C-g-PAN, surface morphologies of them are compared by using SEM technique. SEM photographs of Un-C, C-g-PAN69, and AO2.42-C-g-PAN69 are shown in Figure 1. Un-C has a reasonably smooth surface. On the other hand, C-g-PAN69 and the AO2.42-C-g-PAN69 have somewhat rough surface. These changes in the surface appearance of the grafted and amidoximated samples are caused by the grafting and amidoximation processes.
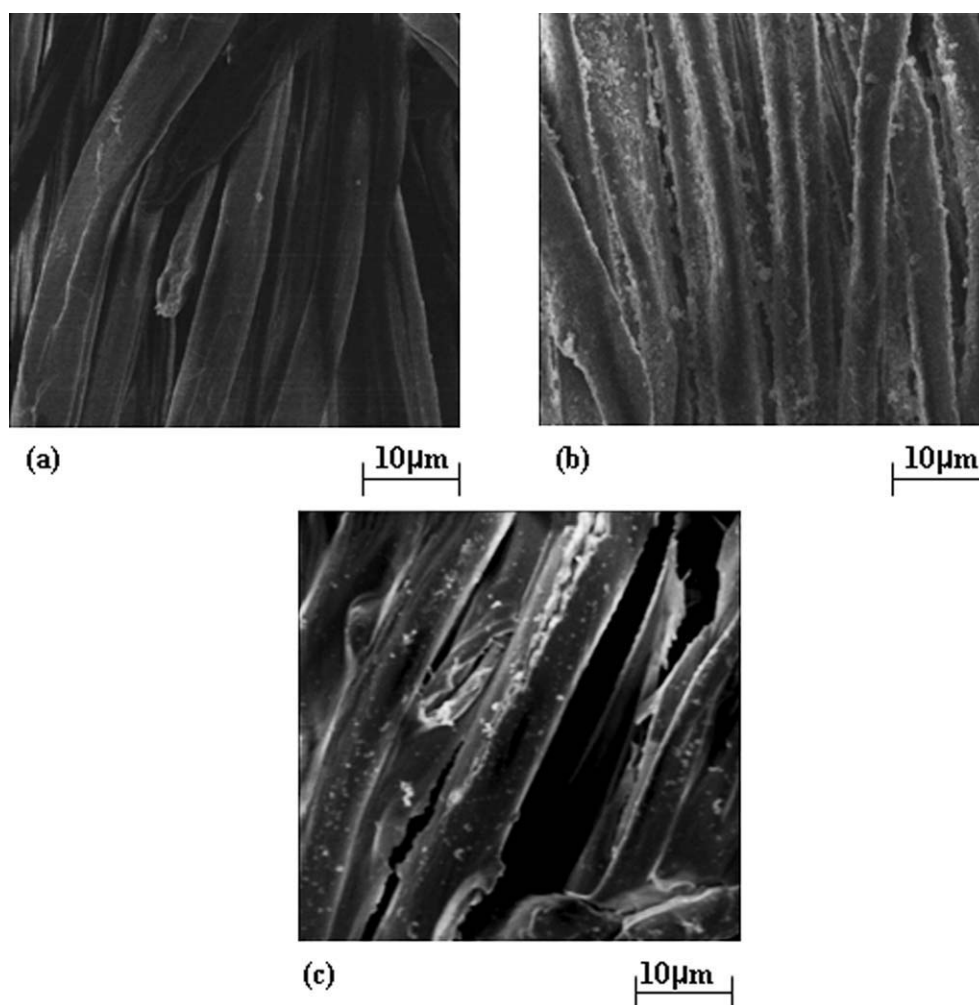
Figure 1   SEM micrographs of Un-C (a), C-g-PAN69 (b), and AO2.42-C-g-PAN69 (c).

Amidoximation of C-g-PAN fibers with high GY was performed at different time and temperatures, as summarized in Table I. Nitrogen contents, $N_1\%$ and $N_2\%$ of C-g-PAN and amidoximated samples, respectively, are determined from the elemental analysis. The degree of substitution of the grafted cellulose (DS) and the amidoxime (DS'), and the amount of the amidoxime (C_A mmol/g) were calculated by using the following relations:

$$DS = M_{\mathrm{glub}}N_1/(100M_N - M_{AN}N_1)$$
$$DS' = (N_2 - N_1)(M_{\mathrm{glub}} + M_{AN}DS)/$$
$$(100M_N - M_{\mathrm{NH_2OH}}[N_2 - N_1])$$
$$C_A = [(N_2 - N_1)/M_N]$$

where M_{glup} is the molecular weight of the glucopyranose unit (162 g); M_N, the atomic weight of nitrogen (14 g); M_{AN}, the molecular weight of AN (53 g); and $M_{\mathrm{NH_2OH}}$, the molecular weight of hydroxylamine (33 g).

As shown in Table I, the amidoximation reaction temperature of 80°C (boiling point of the hydroxylamine solution) provided the higher C_A rather than other temperature examined (60–90°C). At 80°C, the reaction time showed a maximum C_A at 5 h. At longer reaction time, amidoxime groups may be introduced onto the substrate, which leads to cyclization between amidoxime groups and that between amidoxime groups and the nitrile groups, resulting in decrease of C_A.[30]

Figure 2 represents the FTIR spectra of C-g-PAN69, AO1.38-C-g-PAN69, AO2.05-C-g-PAN69, and AO2.42-C-g-PAN69. In the IR spectrum of C-g-PAN69, the strong band observed at 2243 cm^{-1} can be attributed to the stretching vibration mode of the nitrile groups. Absorption bands observed at 839 cm^{-1} and 751 cm^{-1} are due to the rocking motion of methylene groups in PAN chain. After the amidoximation, the amidoxime group was inserted to the PAN grafted copolymer, so that the CN band at 2243 cm^{-1} decreased and disappeared with increasing C_A value in the amidoximated sample, where

TABLE I
Influence of Selected Reaction Parameters in the Preparation of the Amidoximated Grafted Cellulose from Cellulose-Graft-Polyacrylonitrile

C-g-PAN69					Amidoximated grafted cellulose		
GY (%)	N_1^a (%)	DS	Temperature (°C)	Time (h)	N_2^a (%)	DS'	C_A (mmol/g)
69.3	11.23	2.26	60	5	12.32	0.225	0.779
			70	5	13.16	0.407	1.38
			80	5	14.62	0.742	2.421
			90	5	12.86	0.341	1.16
			95	5	12.27	0.215	0.743
			80	2	12.94	0.359	1.221
			80	3	14.10	0.619	2.05
			80	5	14.62	0.742	2.421
			80	10	13.28	0.434	1.464
			80	16	12.74	0.315	1.079
			80	24	11.98	0.154	0.536
49.1	10.67	2.06	80	2	11.63	0.190	0.686
			80	3	12.29	0.326	1.157.
			80	5	12.92	0.460	1.610
			80	10	11.65	0.194	0.700
			80	24	11.04	0.072	0.264

[a] From elemental analysis.
C_A: amidoxime content.

CN band still appears in AO1.38-C-g-PAN69 and then disappeared in AO2.05-C-g-PAN69 and AO2.42-C-g-PAN69 with maximum C_A values. Also, new band appeared in the AO-C-g-PAN, i.e., broad band at 1651 cm^{-1}, corresponding to stretching vibration of C = N and N—OH bonds, overlapping with C—C (ring) stretching vibration and OH in plane binding bands of the cellulose matrix. These results indicate that the conversion of the CN groups to H_2N—C = NOH groups were achieved, which also mean that the hydrophobic nitrile groups are replaced by hydrophilic amidoxime groups.

Figure 3 shows the ^{13}C CP-MAS spectra of C-g-PAN69, AO2.05-C-g-PAN69, and the AO2.42-C-g-PAN69. The resonances belonging to the cellulose (60-110 ppm) are well observed in the all spectra and did not change after the reactions. Also the resonance peaks related to the grafted chain (40 ppm) are observed in the spectrum of C-g-PAN69.[37] In the spectra of the amidoximated grafted cellulose, the peak at 125 ppm, which is related to CN disappeared and a new peak appeared at 152 ppm, corresponding to C=NOH. These results also confirm the change of the nitrile group to amidoxime group without severe damage to the cellulose structure.

Figure 4 shows TGA curves for Un-C, C-g-PAN69, and AO2.42-C-g-PAN69. The first step of the mass loss (rt-150°C) is lower than 5% for C-g-PAN69 and about 7.5% for the AO2.42-C-g-PAN69. In the DSC curves shown in Figure 5, corresponding endothermic peaks at around 90–100°C are observed. The enthalpy of this peak (ΔH) is 76.2 J/g in the C-g-PAN69 which is smaller than that in AO2.42-C-g-
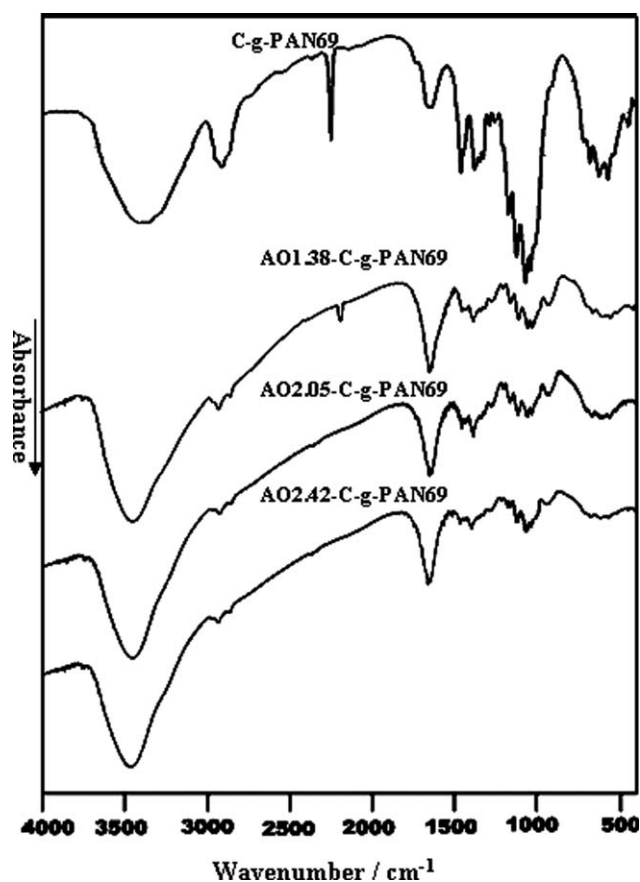

Figure 2 ^{13}C CP MAS NMR spectra of cellulose-graft-polyacrylonitrile (C-g-PAN69), and amidoximated grafted cellulose with C_A of 2.42 and 2.05 mmol/g, respectively, (AO2.05-C-g-PAN69 and AO2.42-C-g-PAN69).
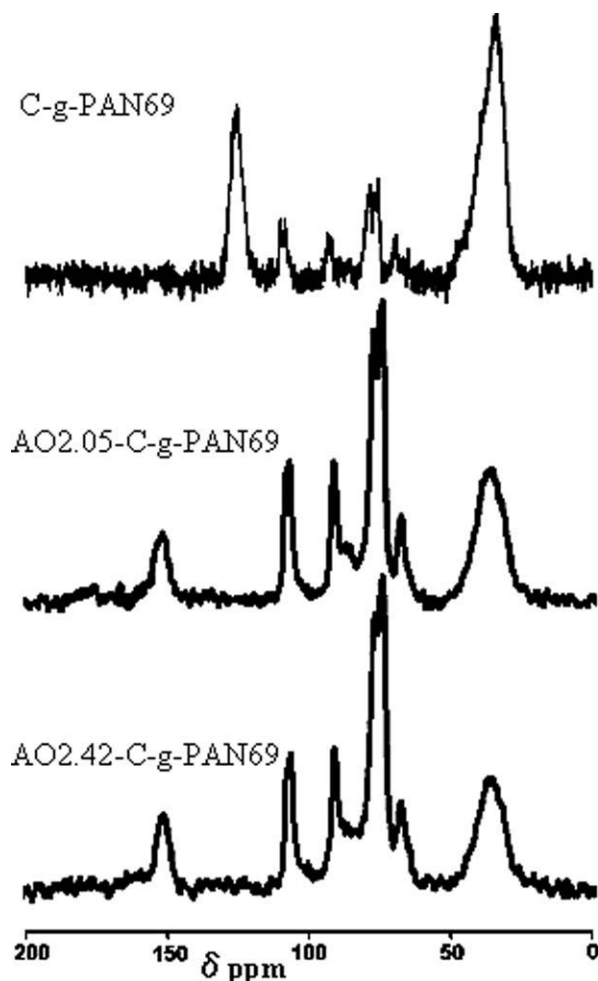
Figure 3 FTIR spectra of C-g-PAN69 and amidoximated grafted cellulose with C_A = 1.38, 2.05 and 2.42 mmol/g, respectively, (AO1.38-C-g-PAN69, AO2.05-C-g-PAN69, and AO2.42-C-g-PAN69).

PAN69 (ΔH = 284.3 J/g) referring to high adsorption water with the amidoxiation reaction in consistent with TGA results. That is, the increase in the mass loss can be attributed to the moisture desorption and the larger value for amidoximated samples is due to increase of the hydrophilicity by the introduction of hydrophilic amidoxime and amino groups.

At higher temperature, degradation of polymers takes place in a few different stages. As already discussed in the previous study,[37] about 10% mass loss of C-g-PAN69 at 250-300°C and DSC peak at around 270°C can be attributed to degradation of grafted PAN. At 300–370°C, mass loss becomes steeper since degradation of cellulose also occurs. Corresponding DSC peak is observed at around 370°C. The amount of residue at 550°C is 46%.

TGA and DSC curves of the amidoximated sample are similar to those of C-g-PAN. However, since the degradation process involves decomposition of the amidoximated group, mass loss starts at around 200°C
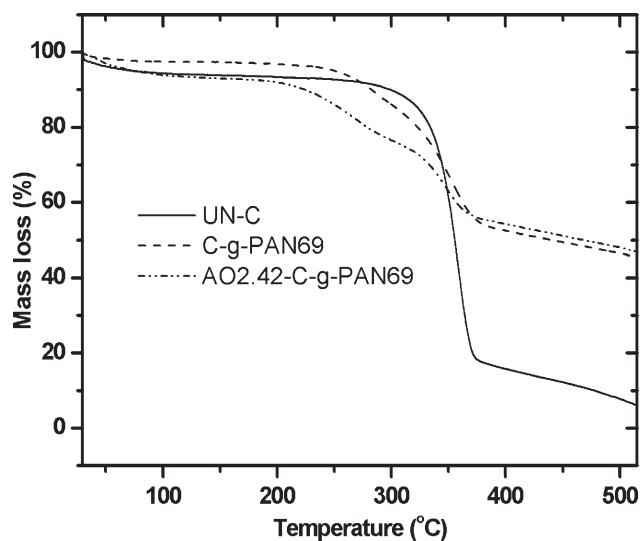
Figure 4 TGA curves of Un-C, C-g-PAN69, and the amidoximated grafted cellulose with C_A = 2.42 (AO2.42-C-g-PAN69).

and corresponding DSC peak slightly shift to lower temperature and become broader. The amount of residue at 550°C is 48%, close to that of C-g-PAN. This result is also consistent with the conclusion in the previous study; residue depends on GY. From these results, we can conclude that the hydrophilicity
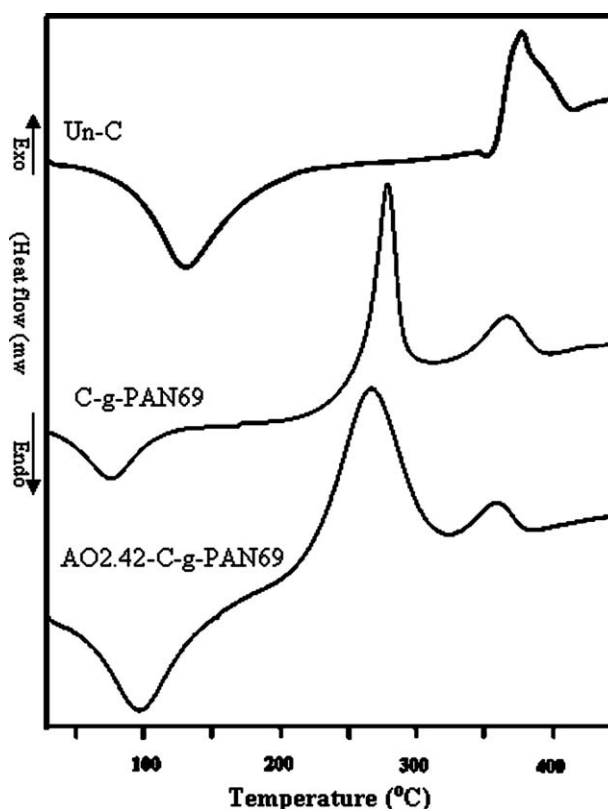

Figure 5 DSC thermograms of Un-C, C-g-PAN69, amidoximated grafted cellulose (AO2.42-C-g-PAN69).
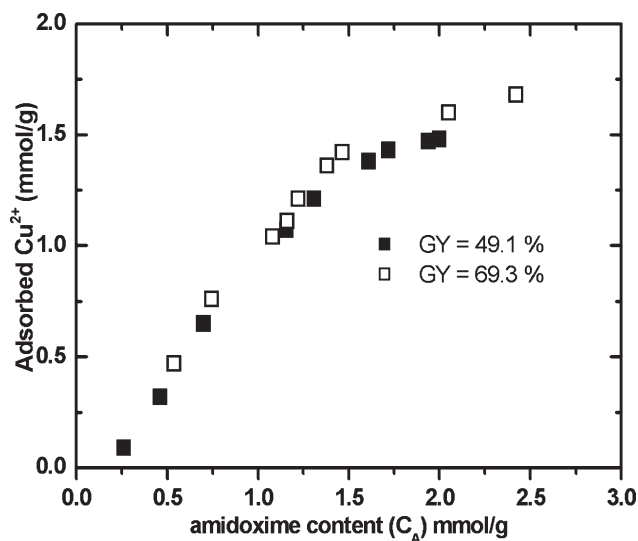
Figure 6 Relationship between adsorbed amount of Cu^{2+} and amidoxime content of the amidoximated grafted cellulose. *DS* of the grafted cellulose: (■) 2.06, (□) 2.26. $[Cu^{+2}]$ = 7 mmol/L, time = 24 h, pH = 5.5, and T = 30°C.

of cellulose fiber increases and thermal stability decreases with the amidoximation reaction.

Adsorption of the heavy metal ions

The conditions of metal ions adsorption test from the aqueous solution by the modified cellulose samples were examined by the following preliminary tests. First, the influence of the soaking time was examined at 4–48 h and found that the adsorption of the metal ions (Cu^{2+}, Co^{2+}, and Ni^{2+}) increased up to 24 h then gradually increased till reached the equilibrium at 36 h. Effect of pH was examined at 2 to 6.5 and found that in the case of Cu^{2+} and Ni^{2+}, the adsorption amount of the metal ion increased with the pH value, whereas the adsorption of Co^{2+} showed no pH dependence within the pH range examined. When the pH was higher than 5.5, precipitation of the Cu^{2+} was observed. Hence, the following experiments were carried out at pH 5.5 and 24 h as best condition for the metal ion adsorption.

Figure 6 represents amidoxime content (C_A) dependence of adsorbed amount of Cu^{2+} ions for 2 samples with different GY. It is clear that adsorbed amount of metal ions increase almost linearly with C_A irrespective of GY up to C_A = 1.4 mmol/g. With further increase of concentration, the adsorbed amount seems to gradually reach equilibrium at high concentration. Note that the number of Cu^{2+} ions in the test system is about 10 times larger than that of amidoxime at high concentration. For semi-quantitative analysis, adsorption of a few different metal ions is tested for AO2.42-C-g-PAN69, which contains 2.42 mmol/g of amidoxime group, in comparison with Un-C and C-g-PAN69 as discussed below.
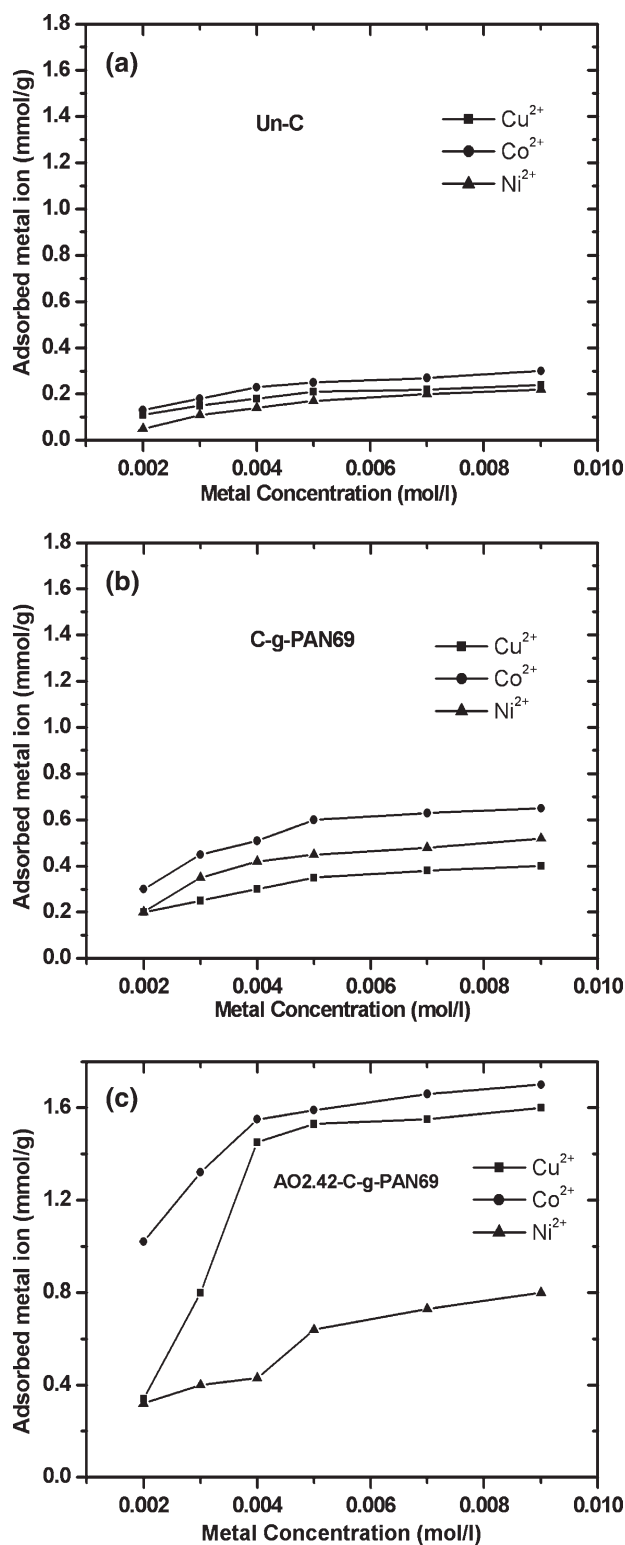

Figure 7 (a) Adsorption of the metal ions with untreated cellulose at time = 24 h, pH = 5.5, and T = 30°C. (b) Adsorption of the metal ions with C-g-PAN69 at time = 24 h, pH = 5.5, and T = 30°C. (c) Effect of the metal concentration on the adsorbed amount of metal ions on amidoximated grafted the cellulose (AO2.42-C-g-PAN69) for 24 h at 30°C and pH = 5.5.

The amounts of the metal ions adsorbed from the aqueous solutions by Un-C, C-g-PAN69, and AO2.42-C-g-PAN69 are shown in Figure 7(a–c), respectively. Hydroxyl group in Un-C can act as an adsorbing site. As shown Figure 7(a), the adsorbed amount of ions by Un-C become almost constant (0.2–0.3 mmol/g) irrespective of the metal species when concentration of metal ion solution exceed 5 mM. C-g-PAN69 [Fig. 7(b)] adsorbs about twice amount of metal ions compared to Un-C, denoting that side chain nitrile group more efficiently adsorb metal ions than main chain hydroxyl group. A weak selectivity of metal ion species is observed for C-g-PAN69.

In contrast to these two samples, AO2.42-C-g-PAN69 adsorbs a large amount of metal ions as shown in Figure 7(c). It is clear that this sample is less effective for adsorption of Ni^{2+}. Adsorbed amount of Cu^{2+} and Co^{2+} ions steeply increases with increase of concentration, up to 5 mmol/L. With further increase of concentration, adsorbed amount of ions seem to approach the equilibrium. The amount of adsorbed Cu^{2+} and Co^{2+} are 1.6 and 1.7 mmol/g, respectively, at the highest metal ion concentration. If we assume that about 0.3–0.4 mmol/g metal ions are adsorbed by cellulose fiber (hydroxyl group) and residual nitrile group, then the molar ratio of amidoxime and metal ions adsorbed by amidoxime is close to full saturation condition (2 : 1).

Comparing with the previous studies,[29–36] we can point out that the adsorbed amounts of metal ions in this study are higher than those reported in the previous works[29–33] even for the samples with similar or higher C_A (0.6 mmol/g and 1.2 mmol/g of Cu^{2+} ion, respectively). Although the detailed difference of structure among our sample and those in previous studies cannot be discussed here, we speculate that the adsorption efficiency of the metal ions of the amidoximated grafted cellulose is influenced by the structure of grafted chains, which may differ with the type of initiation systems of the graft copolymerization. From the above results, we conclude that the amidoximated grafted cellulose, prepared by using KMnO$_4$/citric acid redox initiation grafting system, is more efficient than other amidoximated grafted cellulose prepared by different initiation grafting methods.[29–36]

CONCLUSIONS

Amidoximated grafted cellulose was prepared by reacting C-g-PAN with hydroxylamine and the resultant amidoximated grafted cellulose was characterized by SEM, elemental analysis FTIR, solid-state NMR, TGA, and DSC. The most efficient condition of amidoximation reaction was 80°C and 5 h to obtain amidoxated grafted cellulose with the highest C_A = 2.42 mmol/g. The capability of amidoximated C-g-PAN in adsorption of the metal ions was examined with different adsorption conditions. The highest adsorbed amount of Cu^{2+} and Co^{2+} ions are 1.7 mmol/g and 1.6 mmol/g, respectively, reaching to the adsorption equilibrium at the highest metal ion concentration. It is confirmed that amidoximated grafted cellulose acts as a good metal ion adsorbent compared with Un-C and C-g-PAN as expected. Also comparing with the previous studies,[29–36] we can conclude that the efficiency of the amidoximated grafted cellulose toward the adsorption of the metal ions is influenced by the type of initiation systems of the graft copolymerization which may result in the structure of the absorbent material. As a result, the adsorption efficiency of amidoximated grafted cellulose was improved through the grafting of AN onto cellulose by using KMnO$_4$/citric acid redox initiation system.

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