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Improved Method for Preparation of Amidoxime Modified Poly(acrylonitrile-*co*-acrylic acid): Characterizations and Adsorption Case Study

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Abstract: Redox polymerization of poly(acrylonitrile-*co*-acrylic acid) (poly(AN-*co*-AA)) is performed at 40 °C under N_2 gas by varying the ratio of acrylonitrile (AN) and acrylic acid (AA) in the feed. The yield production of poly(acrylonitrile) (PAN) is 73% and poly(AN-*co*-AA) with a feed ratio of 93:7 is the highest yield (72%). The PAN and poly(AN-*co*-AA) are further chemically modify with hydroxylamine hydrochloride. The FTIR spectroscopy is used to confirm the copolymerization of poly(AN-*co*-AA) and chemical modification of poly(AN-*co*-AA). Elemental microanalysis shows that the overall trend percentage of carbon, hydrogen, and nitrogen for all feed ratios are slightly decreasing as the feed ratio of AA is increasing except for poly(AN-*co*-AA) 93:7. The SEM images shows that spherical diameter of poly(AN-*co*-AA) is smaller compared to the PAN and amidoxime (AO)

modified poly(AN-*co*-AA). The TGA (thermogravimetric analysis) analysis reveals that the poly(AN-*co*-AA) degrades at lower temperatures compared to the PAN but higher than AO modified poly(AN-*c*o-AA). The case study adsorption test showed that the AO modified poly(AN-*co*-AA) 93:7 had the highest percentage removal of Cd^{2+} and Pb^{2+}.
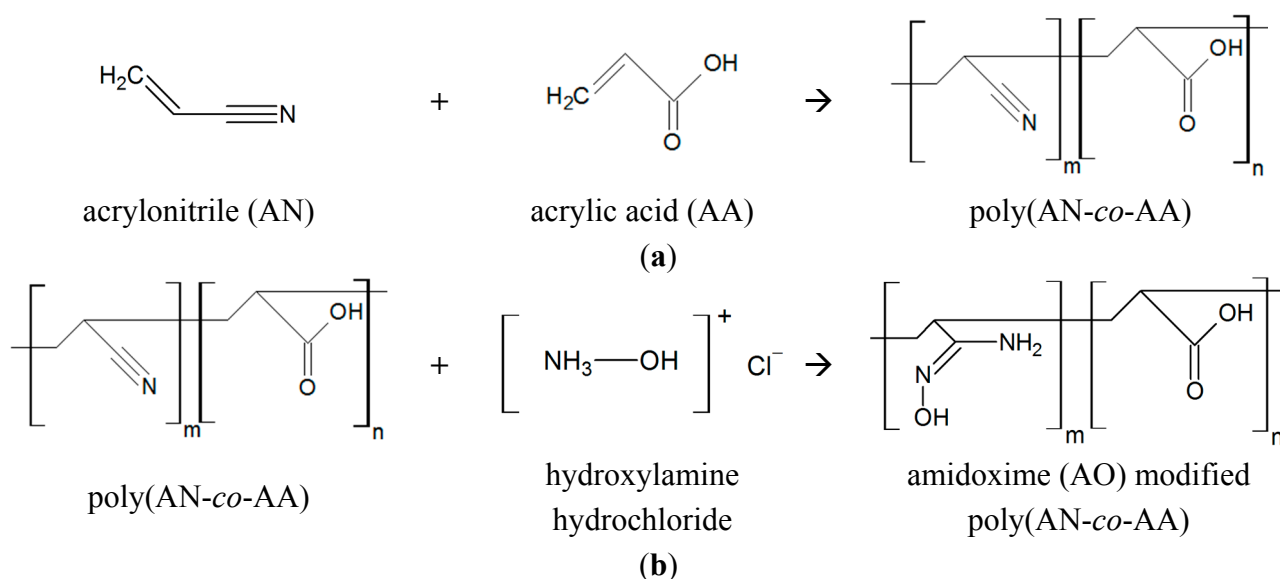
1. Introduction

Acrylonitrile (AN) has been a subject of interest among researchers for many decades. Poly(acrylonitrile) (PAN) has good resistance to organic solvents, is excellent in mechanical strength with high thermal stability (~200 °C) [1]. PAN was introduced in many applications such as in carbon fibers manufacturing for military, sports and aerospace equipment, clinical uses, and synthetic fibers in a modern textile process [1,2]. The utilization of PAN in wide range of applications is due to the existence of reactive cyano group that can be converted into a particular functional group based on certain applications [3,4]. The high nitrile-nitrile dipolar interaction in PAN resulted in low moisture absorption, hydrophobicity and lack of active functionality [1]. Therefore, to weaken the dipole-dipole interactions and improve the hydrophilicity of PAN, the AN was copolymerized with vinyl and acrylic monomers [1,3]. In this current study, acrylic acid (AA) was chosen as a monomer in order to introduce a carboxyl functional group (–COOH) into PAN system. The existence of –COOH in a poly(acrylonitrile-*co*-acrylic acid) (poly(AN-*co*-AA)) overcome the hydrophobicity and nitrile-nitrile interactions; consequently producing pervaporation and antifouling properties for wastewater treatment [1]. Apart from that, AA promotes strong adhesive properties for modification of poly(AN-*co*-AA) which is that only the desired functional group will be replaced and the biocompatibility behavior allow poly(AN-*co*-AA) to be modified with various modification agent [5]. The advantages of redox synthesis are less solvent usage, shorter reaction time, and ability to produce high recovery of polymers [6].

Hydroxylamine hydrochloride is chosen in this present work as modification agent due to capability of amidoxime (AO) group to form high complexity-forms with metal ions [4]. The conversion of nitrile to AO groups enhance the heavy metal ions sorption ability of the poly(AN-*co*-AA). The AO polymer adsorbents have high uptake and selectivity of heavy metal ions, fast adsorption rate, and are easy to manage [7]. The AO containing adsorbents are environmental friendly due to their versatility in regenerated and reused heavy metal uptake purposes [8–9]. Recently, Igberase and Osifo (2014) studied the grafted polymer adsorbent of polyaniline cross-linked chitosan beads in removing cadmium (II) and lead (II) [10]. O'Connell *et al.* (2008) [11], on the other hand, reported the polymer adsorbent of cellulose-acrylic acid in removing lead (II), copper (II) and cadmium (II). The adsorption capacity obtained was 55.9, 17.2 and 30.3 mg·g^{-1} for lead (II), copper (II) and cadmium (II) respectively at pH 4.5.

Generally, most of the studies in producing AO modified polymer resin involved tedious methods with long reaction times that are not feasible to be applied in an industrial scale [4,8,12]. Therefore, in the present work, we make several noteworthy contributions to the high recovery of poly(AN-*co*-AA) with more feasible conditions of redox polymerization as water was adopted as the reaction medium

under mild condition [2,13]. The modification of poly(AN-*co*-AA) with hydroxylamine hydrochloride involved less chemical consumption with a short reaction time.

The aim of this research is to polymerize PAN and poly(AN-*co*-AA) via redox method, to modify the PAN and poly(AN-*co*-AA) with the most efficient method (in terms of modification time, temperature and process facilitation) and to study the preliminary removal cadmium ions (Cd^{2+}) and lead ions (Pb^{2+}) as a case study in adsorption application. Scheme 1a shows the polymerization of AN with AA to form poly(AN-*co*-AA). Scheme 1b shows the modification of poly(AN-*co*-AA) with hydroxylamine hydrochloride to form AO modified poly(AN-*co*-AA). For future studies, it is expected that the AO modified poly(AN-*co*-AA) will be useful for heavy metal ions uptake via complex formation in square planar form.

acrylonitrile (AN)   acrylic acid (AA)   poly(AN-*co*-AA)

(a)

poly(AN-*co*-AA)   +   hydroxylamine hydrochloride   →   amidoxime (AO) modified poly(AN-*co*-AA)

(b)

Scheme 1. (a) Polymerization of poly(acrylonitrile (AN)-*co*-acrylic acid (AA)) and **(b)** Modification of poly(AN-*co*-AA) with hydroxylamine hydrochloride (NH$_2$OH·HCl) resulted amidoxime (AO) modified poly(AN-*co*-AA).

2. Experimental Section

2.1. Materials and Methods

Acrylonitrile (R&M Chemical, Essex, UK) and acrylic acid (MERCK, Darmstadt, Germany) were purified by using aluminium oxide (MERCK, Darmstadt, Germany) to remove impurities. Sodium bisulphate (SBS) (Systerm ChemAR, Shah Alam, Malaysia) and potassium persulphate (KPS) (Systerm ChemAR, Shah Alam, Malaysia) were used as initiators. Deionized (DI) water was adopted as the reaction medium. Methanol (MeOH) was purchased from Systerm ChemAR (Shah Alam, Malaysia). Hydroxylamine hydrochloride (NH$_2$OH·HCl) (Systerm ChemAR, Shah Alam, Malaysia) was used to modify the polymer. Sodium bicarbonate (NaHCO$_3$) (Systerm ChemPur, Shah Alam, Malaysia) and sodium hydroxide (NaOH) (Systerm ChemAR, Shah Alam, Malaysia) were used to adjust the pH during chemical modification of poly(AN-*co*-AA). Hydrochloric acid (HCl) (Fisher Scientific, Loughborough, UK) was used to convert amidoxime (AO) modified poly(AN-*co*-AA) to ammonium form.

2.2. Instrumentation

Scanning electron microscope (SEM) micrographs were acquired using a Hitachi S-3400N instrument (HitachiHigh-Technologies Corporation,Minato, Tokyo, Japan) and were operated at 10 to 20 kV. Samples were coated in Au/Pd film prior to analysis. Fourier transform infrared (FTIR) analysis was recorded on a Perkin Elmer, 1750X Fourier Transform Infrared spectrometer (PerkinElmer Inc., Waltham, MA, USA) by using potassium bromide (KBr) pellets in resolution range of 4000–400 cm^{-1} at room temperature. The elements content (carbon, hydrogen and nitrogen) were calculated using C-31 Microbalance (Cahn Instruments, Inc., Cerritos, CA, USA) and LECO CHNS-932 spectrometer (Leco Corporation, St. Joseph, MI, USA) for weighed and combustion of the sample respectively. The thermogravimetric analysis (TGA) was evaluated using Perkin Elmer, STA 6000 Simultaneous Thermal Analyzer instrument (PerkinElmer Inc., Waltham, MA, USA) from 50 to 1000 °C at 10 °C·min^{-1} under nitrogen atmosphere.

2.3. Polymer Synthesis

Redox polymerizations were performed at 40 °C under N$_2$ gas in a three-necked round bottomed flask, fitted with a water condenser. The synthesis involved five different feed ratios of AN:AA which are 100:0, 97:3, 95:5, 93:7 and 90:10. The AN and AA were freshly purified by passing them through a short column of neutral aluminium oxide (AlO$_2$). Initially, the reaction medium (200 mL deionized water) was purged with N$_2$ gas for 30 min. Then, 275 mmol of AN and 29 mmol of AA were added into the reaction medium followed by 20.08 mmol of SBS and 7.94 mmol of KPS. The solution was stirred mechanically at 200 rpm by using egg-shaped magnetic stirrer. The polymerization reaction was allowed for 3 h. The polymer formed was precipitated in methanol for 1 h. The polymer was filtered and washed successively with 50 mL of methanol and 100 mL of deionized water. The polymer was dried in *vacuo* at 45 °C until a constant weight was obtained. The same method was applied to polymerize PAN [2,6,14].

2.4. Modification with Hydroxylamine Hydrochloride

Four different methods have been implemented towards poly(AN-*co*-AA) to find the best method to transform the nitrile into AO groups (Scheme 1b). The differences between previous study and refined methods are tabulated in Table 1.

Table 1. Amidoxime (AO) modification methods procedure.

Method	Refined Method	Method Differences		Advantages
		Previous	**Refined**	
1	0.375 g of hydroxylamine hydrochloride and 0.375 g of sodium hydroxide were diluted with deionized water in a 50 mL beaker together with 0.025 g of poly(AN-*co*-AA). The mixture was kept for 2 days at room temperature. Then, the poly(AN-*co*-AA) was filtered, washed, and dried at 60 °C.	The mixture was continuoslystirred for 2 days [12].	The mixture was soaked for 2 days.	Less energy consumption.

<div align="center">**Table 1.** *Cont.*</div>

Method	Refined Method	Method Differences		Advantages
		Previous	**Refined**	
2	0.5 M of hydroxylamine hydrochloride (HH) was adjusted to pH 6 by sodium bicarbonate. The mixture was heated and stirred at 70 °C and 80 rpm respectively. 0.250 g of poly(AN-*co*-AA) was added and allowed to react for 1 h. Then,the poly(AN-*co*-AA) was filtered, washed, and dried at 60 °C.	The HH needed was 1.2 M for 0.20 g polymer [15].	The HH needed was 0.5 M for 0.25 g polymer.	Less usage of chemical.
3	0.10 g of sodium hydroxide and 0.17 g of hydroxylamine hydrochloride were mixed with 50 mL of deionized water and 0.10 g poly(AN-*co*-AA). The mixture was kept at 50 °C for 2 h. Then, the poly(AN-*co*-AA) was filtered, washed, and dried at 60 °C.	The reaction time was 2 days [12].	The reaction time was 2 h.	Less time reaction.
4	1.0 g of poly(AN-*co*-AA), 25 mL of methanol and 3.0 g of hydroxylamine hydrochloride were mixed and stirred for 2 h at room temperature. Then, 1.8 g of sodium hydroxide was diluted in 6 mL of deionized water and added into the mixture to neutralize hydrochloric acid and kept at pH 8. The mixture was refluxed for 4 h at 70 °C. Then, the poly(AN-*co*-AA) was filtered, washed, and dried at 60 °C.	The reaction was refluxed for 20 h [4].	The reaction was refluxed for 4 h.	Less usage of energy and short reaction time.

2.5. Amine Capacity

0.1 M of hydrochloric acid (HCl) and 0.3 g of AO modified poly(AN-*co*-AA) were mixed and shook for 4 h to convert polymer into ammonium form. Then, the ammonium form obtained was filtered, rinsed, and dried. The 0.08 g of dry ammonium form and 0.1 M of sodium hydroxide (NaOH) were mixed and shook for 4 h. Then, one drop of phenolphthalein was added into the 10 mL aliquots of supernatant solution. The solution was back titrated with 0.1 M HCl until the end point of phenolphthalein. The volume of HCl used was recorded [3]. The amine capacity was calculated by using Equation (1).

$$\text{Amine capacity} = \frac{V_{HCl} \times M_{HCl}}{W_A} \tag{1}$$

where Amine Capacity is in $mmol \cdot g^{-1}$; V_{HCl} represent volume of HCl used (mL); M_{HCl} is molarity of HCL ($mmol \cdot mL^{-1}$); W_A is Weight of ammonium (g).

3. Results and Discussion

3.1. Synthesis of Polymer

The yield percentage of PAN and poly(AN-*co*-AA) are shown in Figure 1. PAN has the highest yield (73% ± 0.5%) due to the non-incorporation of comonomer that may interrupt the polymerization reaction [2,13]. However, the yield percentage of poly(AN-*co*-AA) 97:3 is lower at 64% ± 1.4%. The amount of AA (contain –COOH functional group) was probably inadequate to form polymer chains and consequently produced low yield. As the amount of AA increased to 5 mol% and 7 mol% ratios in feed, the yields were increased to 71% ± 0.5% and 72% ± 1.6%, respectively. However, as the amount of AA increased to 10 mol% ratios in feed, the yield decreased to 62% ± 1.6%. This is probably due to the excess of –COOH functional groups in polymerization system that retards the formation of polymer chains [2]. In addition, the –COOH functional groups were more reactive than initiating species and easily stabilized the free radical of polymer chain [16]. Thus, the poly(AN-*co*-AA) 93:7 was an optimum ratio in producing high-yield polymer.
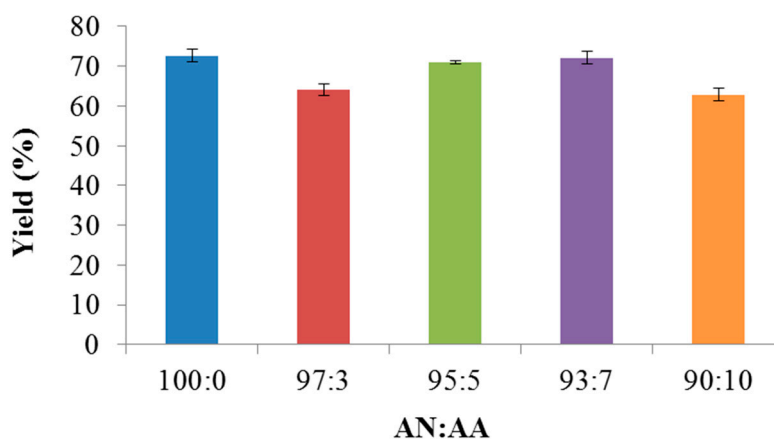

Figure 1. Percentage of yield based on AN (acrylonitrile):AA (acrylic acid) ratios.

3.2. Actual Composition of Comonomer

The actual composition of comonomer between AN and AA was studied due to the yield percentage of polymer for all comonomer feed ratios were less than 95% after polymerization. The actual composition of comonomer for each feed ratio can be calculated using Equations (2) and (3). The optical density ratio (ODR) value was needed in order to reduce the error of physical variations [17]. The ODR can be expressed as [17].

$$ODR = \frac{(Absorbance\ ratio)_{w(C=O)}}{(Absorbance\ ratio)_{w(C\equiv N)}} = \frac{Log(\frac{I_o}{I})_{w(C=O)}}{Log(\frac{I_o}{I})_{w(C\equiv N)}} \tag{2}$$

where I and I_o represent the intensities of the transmitted and incident radiations respectively which can be obtained from the infrared (IR) spectra as shown in Figure 2.
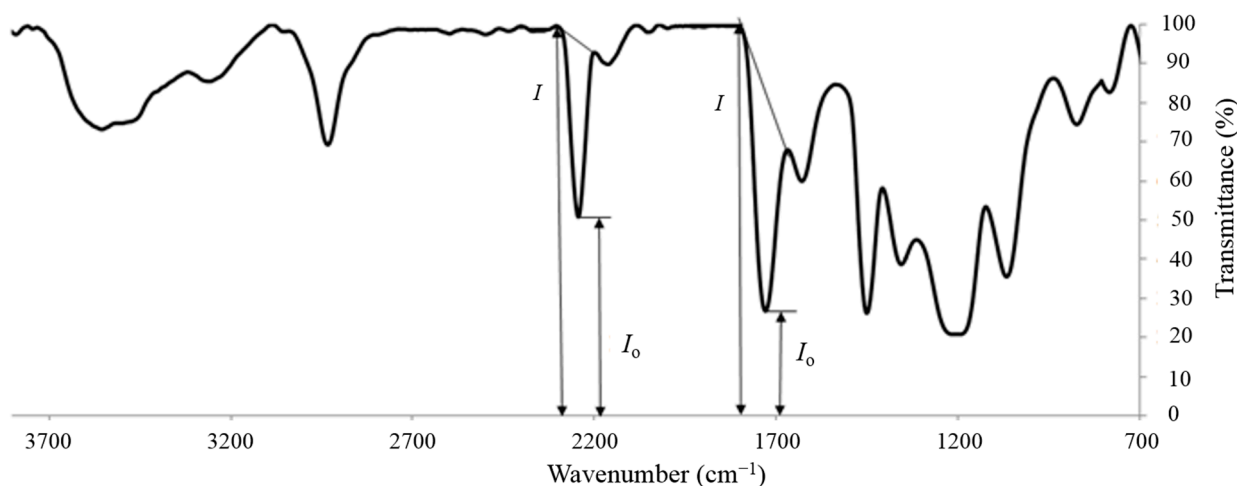
Figure 2. IR spectra of a 93:7 poly(AN-*co*-AA) for ODR (optical density ratio) value. *I* and I_o represent the intensities of the transmitted and incident radiations respectively.

The Equation (3) can be defined as [17].

$$x = 16.3y - 8.5y^2 + 2.24y^3 - 1.78 \tag{3}$$

where *x* is the percentage of AA in the poly(AN-*co*-AA) and *y* is the ODR value. All the comonomer ratios were calculated using Equations (2) and (3) and the results were tabulated in Table 2. Higher incorporation of AA into poly(AN-*co*-AA) indicates that the reactivity of AA is higher compared to the AN monomer. The same observation of high incorporation of AA than AN in polymer chains was reported before [18,19].

Table 2. Comonomer feed and actual composition of comonomer between AN and AA.

Comonomer feed ratio		Actual composition in poly(AN-*co*-AA)	
AN	**AA**	**AN**	**AA**
100	0	100	–
97	3	95	5
95	5	89	11
93	7	85	15
90	10	79	21

In addition, the reactivity ratios for the system were reported as r_1 (AN) = 0.35 and r_2 (AA) = 1.15. The reactivity ratios for AN and AA are r_{12} = 0.40 and r_{21} = 0.40 at the reaction temperature of 50 °C [20]. As the value of monomers r_{12} and r_{21} approach zero, there is higher chances for alternating copolymerization [21] of AN and AA.

3.3. Amine Capacity

The amine capacity was investigated in order to confirm the quantity of AO groups exist in AO modified PAN and poly(AN-*co*-AA). Poly(AN-*co*-AA) with high amine capacity is expected to have better efficiency in adsorption applications [3]. Figure 3 shows that the AO modified poly(AN-*co*-AA) 93:7 has the highest amine capacity (17 mmol·g^{-1}). The AO modified poly(AN-*co*-AA) with the ratios of AN:AA; 100:0, 90:10, 95:5 and 97:3 obtained lower amine capacity which are 15, 14, 12 and

10 mmol·g^{-1} respectively. Higher amine capacity of AO modified poly(AN-*co*-AA) 93:7 compared to PAN and AO modified poly(AN-*co*-AA) 90:10 indicates that incorporation of 7 mol% acrylic acid into the PAN system contributed to the facilitation of chemical modification with hydroxylamine hydrochloride. Most probably, the existence of the optimum amount of carboxylic group along the PAN chains sufficiently reduced the nitrile-nitrile dipolar interaction and consequently, increased the ability of modification and conversion of nitrile groups into AO groups.
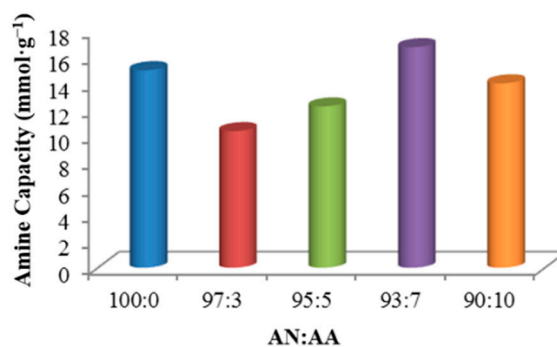

Figure 3. Amine capacity based on AO modified AN:AA ratios.

3.4. Fourier Transform Infrared (FTIR) Spectra

The IR spectra of PAN and poly(AN-*co*-AA) are shown in Figure 4. The absorption band at 2244 cm^{-1} was assigned to the stretching of nitrile groups [22]. The absorption that was assigned to the C=O stretch appeared in all poly(AN-*co*-AA) spectra at bands 1732–1728 cm^{-1}. This indicates that, the AA was successfully copolymerized with AN to form poly(AN-*co*-AA). On the other hand, the absorption bands due to the nitrile stretch in all cases of AO modified poly(AN-*co*-AA) (Figure 4) completely disappeared and were replaced by the appearance of the bands in 1643–1639 cm^{-1} that were assigned to the C=N stretching which overlapped with C=O stretching. In addition, the absorption bands that were assigned to the O-H stretching (2935–2933 cm^{-1}) were shifted to 3332–3197 cm^{-1} and overlapped with N-H$_2$ stretching bands. The bands that were assigned to the N–O stretching from the AO group appeared at approximately 1387 cm^{-1} in all cases of AO modified poly(AN-*co*-AA). The same observation of characteristic bands of AO modified polymer was reported before [23,24].
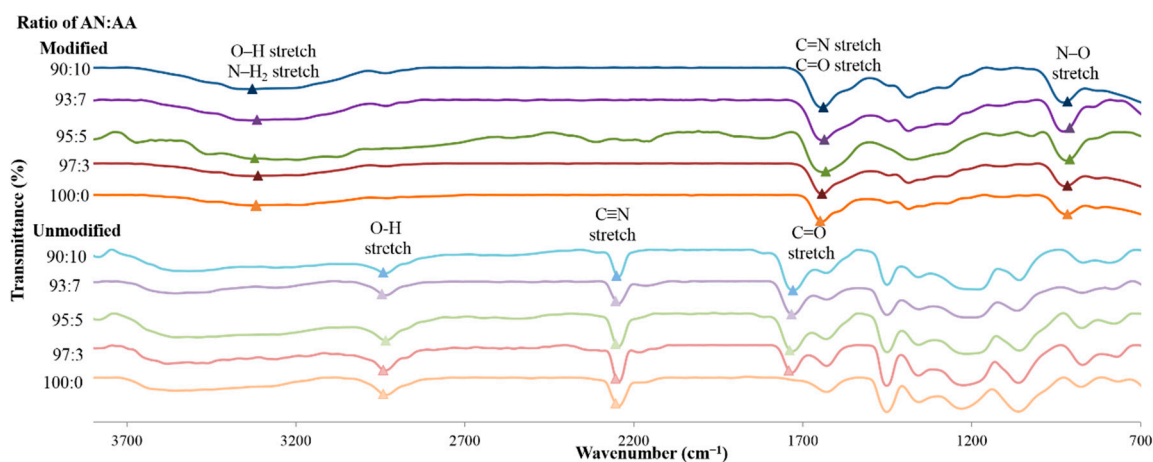

Figure 4. IR spectra of unmodified poly(AN-*co*-AA) and AO modified poly(AN-*co*-AA).

The IR spectra of poly(AN-*co*-AA) 93:7 after modification with four different methods (Table 1) are shown in Figure 5. The disappearance of the band at 2244 cm^{-1} indicates that the nitrile groups have been completely modified with hydroxylamine hydrochloride [4]. All methods were found to successfully modify the nitrile groups except for Method 3; where the nitrile stretch still exists in poly(AN-*co*-AA) after modification. The bands that were assigned to the C=N stretch were observed at 1640 cm^{-1}, 1642 cm^{-1} and 1643 cm^{-1} for Method 1, 2 and 4 respectively. The absorption bands due to the existence of N-O stretch from AO group were appeared at 877 cm^{-1}, 928 cm^{-1} and 902 cm^{-1} in AO modified poly(AN-*co*-AA) that was modified via Method 1, 2 and 4 respectively.
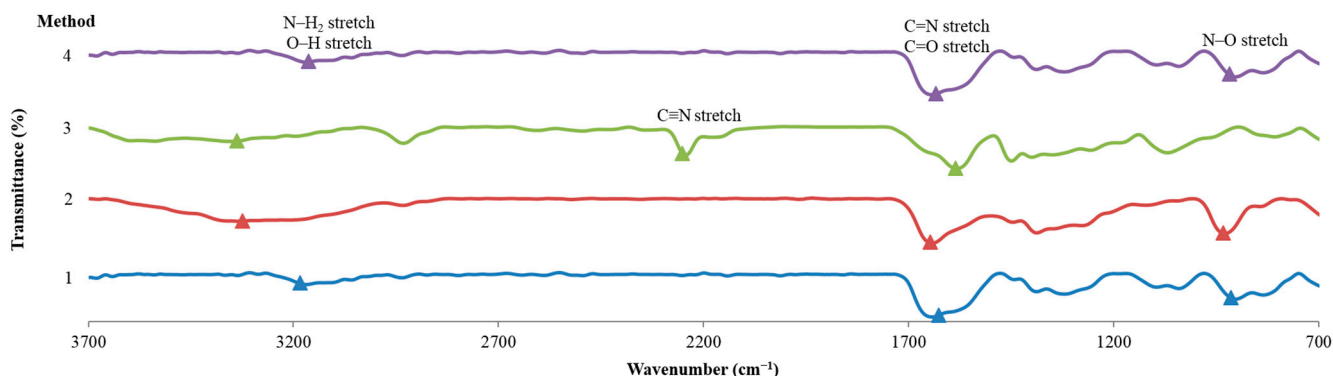

Figure 5. IR spectra of poly(AN-*co*-AA) 93:7 that were modified via different methods.

3.5. Elemental Microanalysis

The analyzed percentage of carbon (C), hydrogen (H) and nitrogen (N) for PAN, poly(AN-*co*-AA), AO modified PAN and AO modified poly(AN-*co*-AA) are tabulated in Table 3.

The unmodified poly(AN-*co*-AA) obtained 64%, 61%, 60%, 63% and 60% of C for the ratios of AN:AA; 100:0, 97:3, 95:5, 93:7 and 90:10 respectively. Similar trends were also observed for the analyzed percentage of H and N. The decreasing of C content and the increasing of H and N content can be observed for all ratios of AO modified poly(AN-*co*-AA). The increasing of N and H content indicate that the nitrile groups in poly(AN-*co*-AA) were successfully converted into AO group. This result was supported by the IR spectra of AO modified poly(AN-*co*-AA) (Figure 4) that showed the appearance of bands that assigned to the N=O and O–H groups at 1387 cm^{-1} and 3332–3197 cm^{-1} respectively.

Table 3. Elemental microanalysis of unmodified poly(AN-*co*-AA) and AO modified poly(AN-*co*-AA).

Ratio of AN:AA		100:0	97:3	95:5	93:7	90:10
Carbon	[a] UM	63.6	61.2	59.9	63.3	59.7
	[b] M	38.8	39.0	40.9	46.0	40.6
Hydrogen	[a] UM	6.8	6.4	6.3	6.9	6.4
	[b] M	7.4	7.4	8.1	8.8	7.2
Nitrogen	[a] UM	24.5	24.1	20.9	21.1	19.4
	[b] M	24.8	24.3	24.3	26.4	22.4

Notes: [a] UM: Unmodified poly(AN-*co*-AA); [b] M: AO modified poly(AN-*co*-AA).

3.6. Scanning Electron Microscopy (SEM)

Figure 6 shows the morphologies of unmodified poly(AN-*co*-AA) (Figure 6a,c,e,g,i) and AO modified poly(AN-*co*-AA) (Figure 6b,d,f,h,j). Generally, agglomerated spherical beads have been formed and similar observations were reported for the polyvinylidene fluoride (PVdF) [25]. The agglomerated character was probably due to the complex formation and interparticle attraction between monomers during polymerization process. The agglomeration also tends to occur due to the solution viscosity and surface behavior of polymer particles [26].
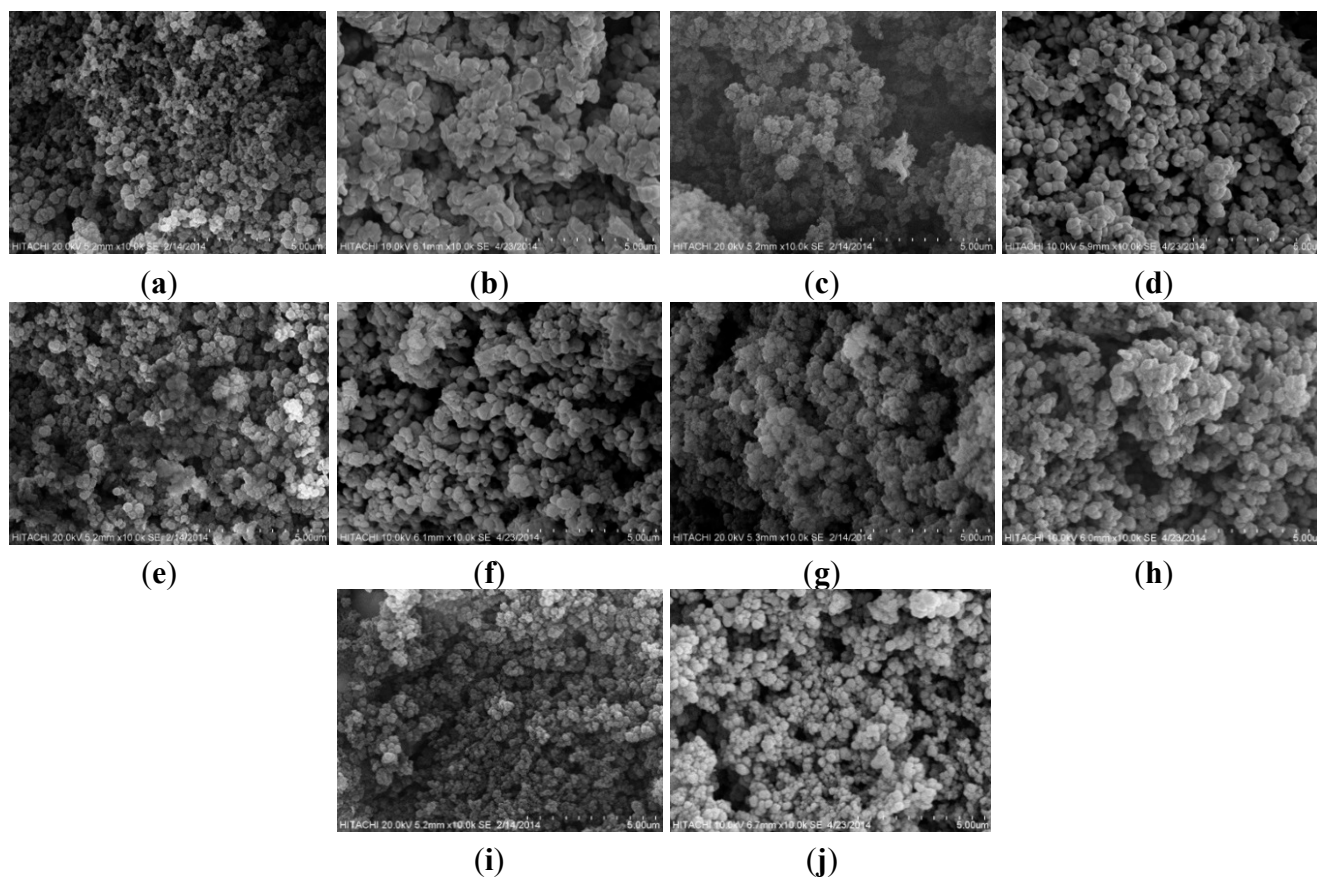

Figure 6. SEM images of (**a**) PAN; (**b**) AO modified (PAN); (**c**) poly(AN-*co*-AA) 97:3; (**d**) AO modified poly(AN-*co*-AA) 97:3; (**e**) poly(AN-*co*-AA) 95:5; (**f**) AO modified poly(AN-*co*-AA) 95:5; (**g**) poly(AN-*co*-AA) 93:7; (**h**) AO modified poly(AN-*co*-AA) 93:7; (**i**) poly(AN-*co*-AA) 90:10 and (**j**) AO modified poly(AN-*co*-AA) 90:10.

As shown in Figure 6, the average particle sizes of poly(AN-*co*-AA) were 216, 178, 159, 130 and 89 nm for the ratios of AN:AA; 100:0, 97:3, 95:5, 93:7 and 90:10 respectively. It was shown that, as the incorporation of AA into the PAN system increased, the average particle size of poly(AN-*co*-AA) significantly decreased. Most probably, as the incorporation of AA increased in the PAN system, the solvation of reaction medium towards the polymer phase becomes poorer. Hence, early phase separation of polymer from the monomer phase occurred and resulted in the reduction of particle size of poly(AN-*co*-AA) [27].

After modification with hydroxylamine hydrochloride, the average particle size of poly(AN-*co*-AA) was increased to 500, 353, 317, 307 and 273 nm for the ratios of AN:AA; 100:0, 97:3, 95:5, 93:7 and 90:10 respectively. The larger average particle size of the spherical beads after modification indicates

that the AO functional group has been introduce into the PAN and poly(AN-*co*-AA). Similar observations were reported for the introduction of AO functional groups in poly(acrylonitrile-methyl acrylate) system [4].

3.7. Thermogravimetric Analysis (TGA)

Figure 7 shows the thermogravimetric (TG) curve and derivative thermogravimetric (DTG) curve for both PAN and poly(AN-*co*-AA) respectively. In the range of 200–400 °C, it was found that the decomposition of poly(AN-*co*-AA) is lower compared to the decomposition of PAN (Figure 7b). Similar cases were reported before [2,28]. This is due to the incorporation of AA in the PAN system that interrupt the nitrile-nitrile unit arrangement in the poly(AN-*co*-AA) chain by the intra or intermolecular interactions resulting in the lower cyclization rate of poly(AN-*co*-AA) compared to PAN [2]. Moreover, the AN units in a polymer chain also play an important role where the higher number in AN units, the higher the initial degradation temperature due to PAN being much more thermally stable [29].
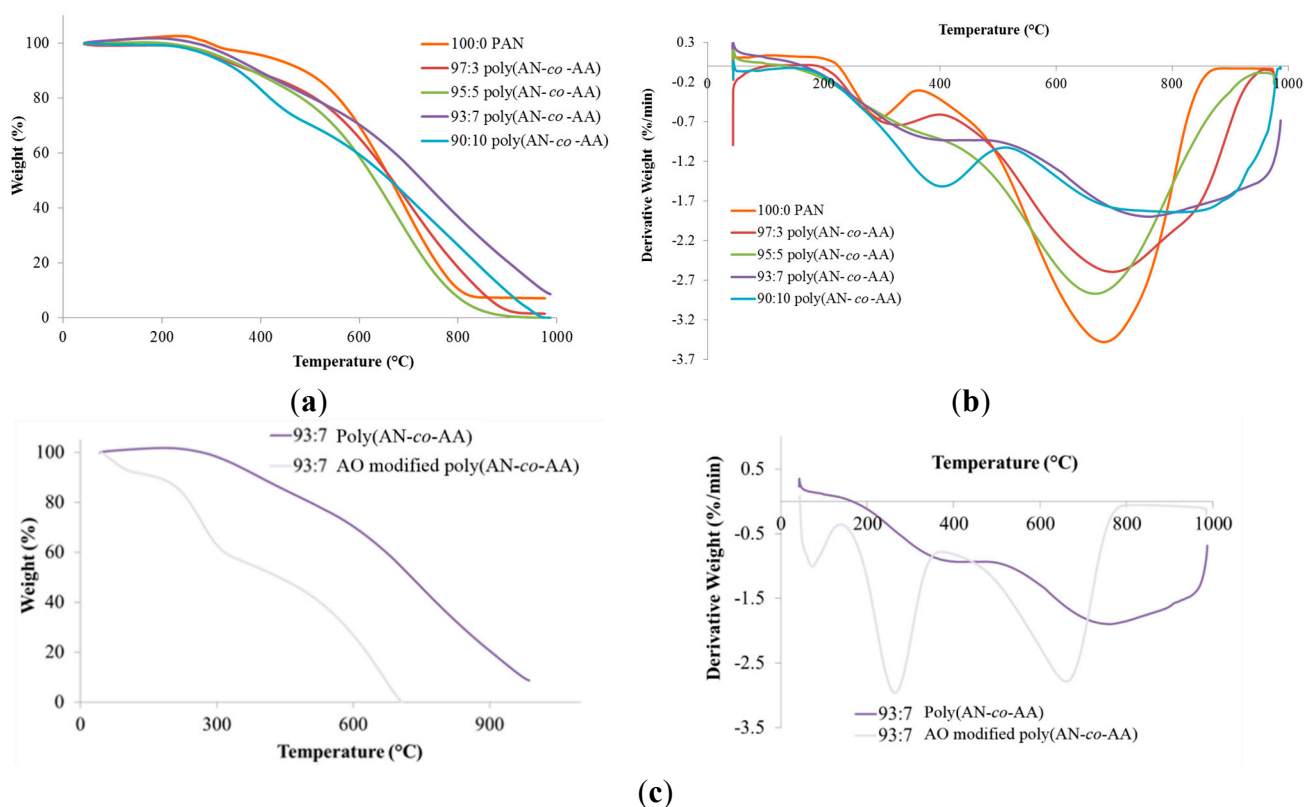

Figure 7. (**a**) TG curve of PAN and poly(AN-*co*-AA) (**b**) DTG curve of PAN and poly(AN-*co*-AA) (**c**) TG and DTG curve of poly(AN-*co*-AA) 93:7 and AO modified poly(AN-*co*-AA) 93:7.

As shown in Figure 7b (in the range of 400–900 °C) PAN has a more intense peak compared to poly(AN-*co*-AA). Similar observations were reported while comparing degradation peak of PAN with poly(acrylonitrile-fumaronitrile) [2,13]. The most broad with less intense peak in the DTG curve is poly(AN-*co*-AA) 93:7 indicating that the degradation occurred at slower rate. This is probably due to the optimum content of carboxylic acid in poly(AN-*co*-AA) 93:7 that facilitated the late complete

breakdown of the polymer chain [30]. In addition, incorporation of 7 mol% of AA provided most favorable steric configuration and consequently improved the thermal stability of poly(AN-*co*-AA) [31].

While comparing the degradation behavior of poly(AN-*co*-AA) and AO modified poly(AN-*co*-AA) in Figure 7c, it was shown that the poly(AN-*co*-AA) fully degraded at ~1000 °C. The DTG curve of poly(AN-*co*-AA) appeared as broad with a less intense peak curve within the temperature of 200 °C until ~1000 °C which indicates that the degradation occurred slowly.

On the other hand, as shown in Figure 7c, AO modified poly(AN-*co*-AA) fully decomposed at temperature ~706 °C. In addition, the DTG curve of AO modified poly(AN-*co*-AA) has a broad degradation curve in the range of 200–400 °C and continues with a second broader degradation curve at 410–800 °C. This is probably due to the existence of hydroxyl groups that immigrate the nitrile groups, which results in a higher cylization rate [31].

AO modified poly(AN-*co*-AA) undergo faster degradation as compared to the poly(AN-*co*-AA); this is probably due to the presence of amidoxime groups along polymer chains that interrupt the stability of poly(AN-*co*-AA). The introduction of new functional groups in the PAN system contributed to the large heat uptake during stabilization process that caused excessive chain scissions. This can be proved by the intense endothermic peak at range 180–400 °C (Figure 7c) that was assigned to the temperature range for the stabilization of PAN [32]. The different degradation behavior of poly(AN-*co*-AA) 93:7 and AO modified poly(AN-*co*-AA) 93:7 is one of the ways to indicate that the modification of poly(AN-*co*-AA) with hydroxylamine hydrochloride was successful.

3.8. Amidoxime (AO) Modified Poly(AN-co-AA)

Hydroxylamine hydrochloride has been widely used as a reducing agent in various resins including PAN by converting the nitrile groups into AO groups [1,10,31]. In this study, the refined methods (convenient and economic methods) for the modification of poly(AN-*co*-AA) system have been achieved by altering some of the methodologies from a previous literature review (Table 1). As shown in the IR spectra (Figure 4), Method 3 was unsuccessful in transforming the nitrile groups into AO groups. This was probably due to the insufficient hydroxylamine hydrochloride concentration during the modification process compared to Methods 1, 2 and 4.

Method 2 was chosen for the modification of poly(AN-*co*-AA) in present work due to the conveniet and economical way of modification; the modification accomplished within 1 h (shorter reaction time compared to Methods 1 and 4). The successful of poly(AN-*co*-AA) modification was confirmed by the IR spectra (Figure 4).

3.9. Case Study on Adsorption Application

The ability of AO modified poly(AN-*co*-AA) to adsorb heavy metal ions of cadmium ions (Cd^{2+}) and lead ions (Pb^{2+}) was initially investigated as a case study (Table 4). As expected from the amine capacity test result, the AO modified poly(AN-*co*-AA) 93:7 will result in the highest percentage removal of heavy metal ions (Cd^{2+}: 38% and Pb^{2+}: 87%) than others. This is due to the high number of amine groups that attract the heavy metal ions. Others than that, considering a better thermal stability of poly(AN-*co*-AA) as compared to the PAN (Figure 7a,b) the utilization of poly(AN-*co*-AA) for further work is more attractive especially for the application of the adsorbent at high temperature. For instance, poly(AN-*co*-AA) has a better

affinity for water due to the existence of –COOH pendant groups contributed by acrylic acid constituent along the polymer chains. In contrast, PAN was known as a hydrophobic polymer due the nitrile-nitrile dipolar interactions along PAN chains [1,3]. Hence, it is expected that the AO modified poly(AN-*co*-AA) 93:7 has high potential to make efficient adsorptions in aqueous solution and waste water.

Table 4. Adsorption test on AO modified poly(AN-*co*-AA) with different ratios of adsorbent.

Ratio AN:AA of AO Modified Poly(AN-*co*-AA)	Cadmium Ions (Cd^{2+})		Lead Ions (Pb^{2+})	
	Percentage Removal, Q_e (%)	Standard Deviation	Percentage Removal, Q_e (%)	Standard Deviation
100:0	21	±0.6	80	±0.8
97:3	15	±0.3	70	±1.1
95:5	21	±0.7	81	±0.7
93:7	38	±0.5	87	±0.2
90:10	24	±1.0	74	±0.5

Initial pH: ≈ 6; Initial concentration, C_o: 100 mg·L^{-1}; Adsorbent dosage, Ws: 2 g·L^{-1}; Agitation speed: 150 rpm; Time: 90 min.

4. Conclusions

PAN successfully produced 73% yield and the highest yield of poly(AN-*co*-AA) was 72% (poly(AN-*co*-AA) 93:7). The previous methods of chemical modification with hydroxylamine hydrochloride were refined to obtain a convenient and economical method for polymer modification. The elemental microanalysis showed that the overall trend percentages of H and N for all feed ratios were increased and satisfied with the IR spectra result by the appearance of N=O and O–H groups after the chemical modification. SEM micrographs showed that the average particle size of AO modified PAN and AO modified poly(AN-*co*-AA) increased as compared to PAN and poly(AN-*co*-AA). The AO modified poly(AN-*co*-AA) degraded at lower temperature compared to poly(AN-*co*-AA). The data obtained from the IR spectra, elemental microanalysis, amine capacity test, SEM micrographs and TGA collaborated and supported each other to prove that the poly(AN-co-AA) were successfully modified with hydroxylamine hydrochloride. The AO modified poly(AN-co-AA) has been tested on removal of Cd^{2+} and Pb^{2+}. The AO modified poly(AN-*co*-AA) 93:7 showed a high percentage removal for both of the heavy metal ions' removal which satisfies all characterization analysis results. Apart from the AO modified polymer having potential applications for various heavy metal uptakes, the poly(AN-*co*-AA) can be applied in applications of blood filtration devices and as biological catalyst.

Author Contributions

Nur Amirah Mohd Zahri performed all the experimental and data analysis; Siti Nurul Ain Md Jamil, Luqman Chuah Abdullah, Thomas Choong Shean Yaw, Sim Jia Huey and Mohsen Nourouzi Mobarekeh

were involved in data analysis; and Nur Salimah Mohd Rapeia was involved in performing synthesis of polymerization.

Conflicts of Interest

The authors declare no conflict of interest.

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