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Synthesis and application of chelating resins based on polyacrylonitrile-diethylenetriamine for metal ions removal

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Abstract

Chelating resins based on polyacrylonitrile and diethylenetriamine (PAN-DTA) were prepared through the simple reaction of polyacrylonitrile with various volume percents of diethylenetriamine (DTA), (25, 50, 75 and 100). The prepared resins were applied to remove heavy metal ions such as Cu(II), Zn(II) and Cd(II) from aqueous solutions. The sorption behaviors of the resins for these metal ions were found to be greater at higher solution pH values. Highest sorption on PAN-DTA was determined as 5 mmol g^{-1} for Cu(II). The number of amine groups present in the resin (amine capacity) is depended on the volume percent of DTA and the maximum capacity was obtained 6.25 mmol g^{-1}. The resins and their metal complexes have been studied by FT-IR spectroscopy, scanning electronic microscopy (SEM) and thermogravimetry analysis (TGA). All these analyses methods confirmed the presence of metal in the metal-resin complexes.

Keywords: Polyacrylonitrile; Diethylenetriamine; Metal ion; Chelating resin.

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1. Introduction

Metal ions especially heavy metals can be introduced into aquatic systems through effluent discharges from various industrial operations including mining, chemicals manufacture, electroplating and distilling and brewing [1, 2]. Although source reduction and efficient waste management programs are the preferred long- term solutions, upgrading existing treatment systems and the implementation of new and novel technologies will continue to play an important role. Numerous processes exist for removing dissolved metals, such as coagulation and chemical precipitation [3], slow sand filters [4, 5], membrane technologies [6-8], adsorbing natural products [9-12] and adsorbing resins [13, 14].

In recent years, there have been many reports of the concentration and separation of trace elements in solutions by using synthesized resins with various organic functional groups because of their large specific surface area and excellent characteristic of adsorbing ions selectively. Many researchers enriched and determined a series of trace rare elements in samples with synthesized chelating resins [15–21].

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A chelating resin based on polyacrylonitrile (PAN) has been chemically prepared through different reactions to obtain different chelate groups. The chemical modifications of cyano groups on the polyacrylonitrile were carried out by reaction with hydroxylamine, 2-amino-2-thiazoline, thiosemicarbazide, ethylenediamine and monoethanolamine to prepare resins that can be used as a very low cost effective sorbent for metal ions [22-26]. Also, the modified PAN fibers were already prepared through the reaction of PAN fibers with multiamine compounds and were used for removal of Pb(II) and Cu(II) [27, 28] but with low metal sorption capacity. The resins used in this work were developed in our laboratory by simple and one-step reaction of PAN powder with diethylenetriamine and triethylenetetraamine [29].

Here in, we report the more details studies on PAN-DTA resins preparation and the batch extraction of Cu, Zn and Cd ions from aqueous solutions for the first time. The synthesis route is rapid, economical and easy to operate, and the functional groups in the resin were verified by FT-IR spectroscopy. The sorption behaviors of the prepared amine containing resins were investigated for Cu(II), Zn(II) and Cd(II) and the sorption capacity of resins for these metal ions were measured with complexometric titration using standard EDTA solutions. PAN-DTA resins and their metal complexes were also studied with scanning electron microscopy (SEM) and thermogravimetery analysis (TGA).

2. Experimental

2.1. Materials and instruments

Polyacrylonitrile was provided by Polyacryl Co. (Isfahan-Iran) with a molecular weight of 60000 g/mol (15% acrylic acid, based on elemental analysis data). Diethylenetriamine (DTA) was purchased from Merck and used without purification. Copper(II) nitrate [$Cu(NO_3)_2.3H_2O$], Zinc(II) nitrate [$Zn(NO_3)_2.6H_2O$] and Cadmium(II) nitrate [$Cd(NO_3)_2.3H_2O$] were provided by Fluka and were used directly. The infrared spectra (4000-500 cm^{-1}) were recorded with Unicom 4600 spectrophotometer by using KBr pellets. The electron micrographs were obtained by using a scanning electron microscope (SEM) LEO 440i. The thermal stability of polymers was studied by a Dupont TGA-951 US thermogravimeter.

2.3. Preparation of PAN-DTA resins

2.3.1. Preparation of PAN-DTA 25, 50 and 75 resins

PAN-DTA25 was prepared by adding a 2.5 g amount of PAN to 25 ml of 25 %(v/v in water) diethylenetriamine solution in a 100 ml round bottom flask. The mixture was stirred on a magnetic stirrer, and the reaction was allowed to proceed at 100-110 °C for 24 h. Then, the resin was separated from solution by filtration, rinsed with distilled water till neutral, dried at 50 °C in an oven overnight, and stored on a desiccators prior to use for the sorption study. PAN-DTA50 and PAN-DTA75 resins were prepared similar to above procedure by using 50% and 75% diethylenetriamine aqueous solutions.

2.3.2. Preparation of PAN-DTA100 resin

The titled resin was prepared by adding a 2.5 g amount of PAN to 25 mL of diethylenetriamine in a 100 mL round bottom flask, and the reaction was carried out at 100-110 °C and 5h. After completion of the reaction while gelation was occurred, some distilled water was added and the resins was separated from solution by filtration, rinsed with distilled water till neutral, dried at 50 °C in an oven overnight, and stored in desiccators prior to use for the sorption study.

2.4. Sorption of Cu(II), Zn(II) and Cd(II) ions

Batch sorption experiments were conducted in 50 ml beakers, each of them contained 30 ml of a metal solution prepared with 2 mmol of $Cu(NO_3)_2$. $3H_2O$ (483mg) or Zn $(NO_3)_2.6H_2O$ (595mg) or $Cd(NO_3)_2.3H_2O$ (650 mg) . A 0.1 g amount of PAN-DTA resin was added into the beaker and the contents in the resulting mixture was stirred on a magnetic stirrer. After the completion of reaction, the resins were separated from the solution by filtration, which were rinsed with aqueous solution at the same pH to remove non-complexed metal ions. Then, the metal-resin complexes were dried at 50 °C in an oven.

To investigate the effect of solution pH values with respect to the sorption capacity of PAN-DTA resins, the sorption time was 2 h, the solutions pH values were changed from 1 to 4.5 for Cu(II), 1 to 6.5 for Zn(II) and 2 to 6 for Cd(II). On the other hand, for investigation of the contact time effect on the sorption of selected ions, the solution pH was maintained at maximum value while the sorption time was changed from 10 minutes to 8 hours.

2.5. Amine capacity of PAN-DTA resins

A sample (about 0.5 g) of the PAN-DTA resin was completely converted to the H^+ form by treating the resin with excess solution of 0.1 mol L^{-1} HCl in a beaker for 4 h. The resin was separated from the acidic solution by filtration, rinsed with distilled water until get neutral pH, and then dried at 50 °C. Exactly 0.2 g of the H^+ form of resin was weighed into a 250 ml Erlenmeyer flask and 25 mL of standard 0.1 mol L^{-1} NaOH solution was added to the flask with a stopper and was shaken for about 4 h. After shaking, 10 mL aliquots of the supernatant solution were back-titrated to the phenolphthalein end point with standard 0.1 mol L^{-1} HCl solution.

2.6. Recovery of copper and reuse of the resins

Exactly 150 mg of PAN-DTA resin containing copper was weighed into a 100 ml beaker and 30 mL of 4 mol L^{-1} hydrochloric acid was added into the beaker. The mixture was shaken for 2 h, and then the resin was separated from solution by filtration and eluted with 30 mL of 12.5% aqueous ammonia and washed with distilled water until get neutral pH, and dried at 50 °C to obtain a constant weight. The resin was used again to sorption of copper.

3. Results and discussion

3.1. Preparation of resins

The interaction of diethylene triamine (DTA) with plyacrylonitrile (PAN) and experimental conditions are illustrated in Scheme 1. The prepared amine-containing resins were insoluble in water and common organic solvents, suggesting the formation of a cross-linking structure. Table 1 presents physical and chemical properties of resins.

3.2. Analysis of FT-IR spectra

Fig. 1 shows the FT-IR spectra of the initial PAN and prepared PAN-DTA resins. The peaks for the PAN in Fig.1 (a) can be assigned as follows: 3418.8 cm^{-1} (OH stretching), 2935.5 cm^{-1} (CH stretching), 2247.3 cm^{-1} (C≡N stretching), 1734.5 cm^{-1} (C=O stretching), 1453.2 cm^{-1} (CH bending), 1218.3 cm^{-1} (C-O stretching) and 536.1 cm^{-1} (C=O twisting). After the reaction of PAN with various volume percents of DTA, the spectra of the obtained amine containing resins (Fig.1 (b-d)) show many significant changes. The week peak at 3418.8 cm^{-1} for the PAN was replaced by a strong broad band for the resins. This strong broad band ranging from 3200-3500 cm^{-1} usually corresponds to the combination of the stretching vibration bands of both OH and

NH groups (the identification of the individual contribution of the OH and NH groups is normally not possible due to the overlapping of the vibrating bonds of these two groups in the FT-IR spectrum).

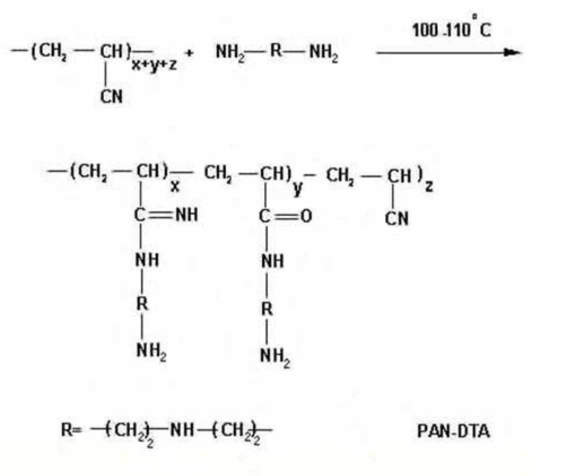
Table 1
Some physico-chemical properties of synthesized resins.

Resin	Physical form and color	Solubility in water	Thermal stability loss at 250°C	Char yield (%) [b]	Yield (%) [c]	Amine content mmol g-1	Nitrogen content mmol g^{-1}
PAN-DTA50	solid, powder yellowish	insolube	18.9 (7.8) [a]	13.3	5.2 (70.65)	4.70	14.2
PAN-DTA100	solid, powder yellowish	insoluble	21.1 (4.4) [a]	12.2	4.2 (57.06)	6.25	16.6

[a] Data after reducing of adsorbed water till 150 °C,

[b] Percentage weight of material left undecomposed after TGA analysis at a maximum temperature of 600 °C in a nitrogen atmosphere

[c] based on 2.5 g PAN



Scheme 1 Synthesis of amine containing resins based on polyacrylonitrile

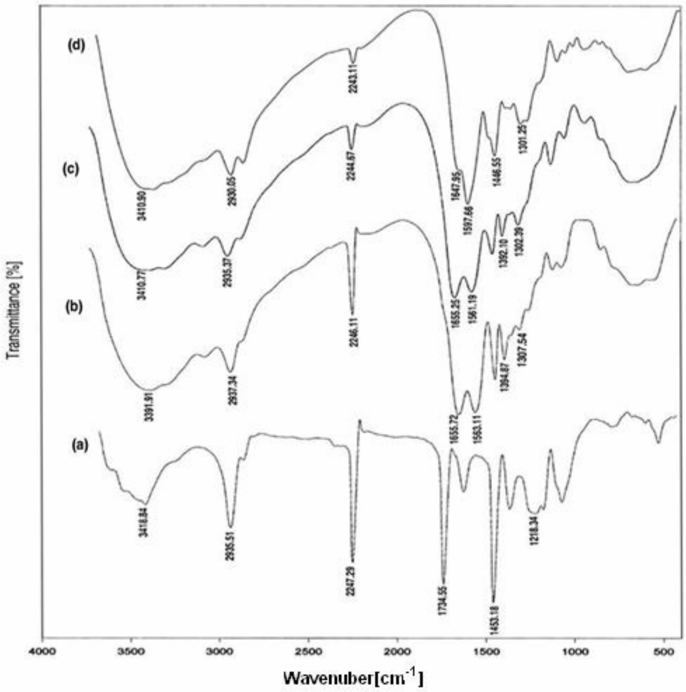


Fig. 1. FT-IR spectra: (a) PAN; (b) PAN-DTA25; (c) PAN-DTA50 and (d) PAN-DTA 100.

On the other hand, the significant reduction of the peak at 2247.3 cm^{-1} for the C≡N groups of the PAN was observed in Fig.1 with increase of volume percent of DTA (the peak at 2247.3 cm^{-1} for the C≡N stretching did not disappear completely, which suggests that only part of the nitrile groups on the PAN were converted during the treatment). In addition, the new bonds observed at 1655.7, 1563.1 and 1394.8 cm^{-1} for the PAN-DTA resins can be assigned to the C=O (or C=N) groups in amide, the N–H group in amine or amide and the C–N group in amide, respectively. These results and other evidences were confirmed the introduction of amine groups in the PAN structure (Scheme 1).

Fig. 2 shows the FT-IR spectra of the PAN-DTA resins together with their Cu(II) complexes. On comparing traces (a) and (b) with (c) and (d) in Figure 1, it can be seen that the peak at 3410.7 cm^{-1} of N–H stretching was displaced towards higher wavenumber after Cu(II) sorption by the resins. Meanwhile, the peak at 1392.1 cm^{-1} of C-N bending was displaced towards lower wavenumbers. These changes occurred may be due to combination of nitrogen atoms in N–H and =N–H, and of oxygen atom in O=C–N with Cu(II) ion to form chelate complex. For other metal resin complexes the same changes of FT-IR characteristic peaks have been observed.

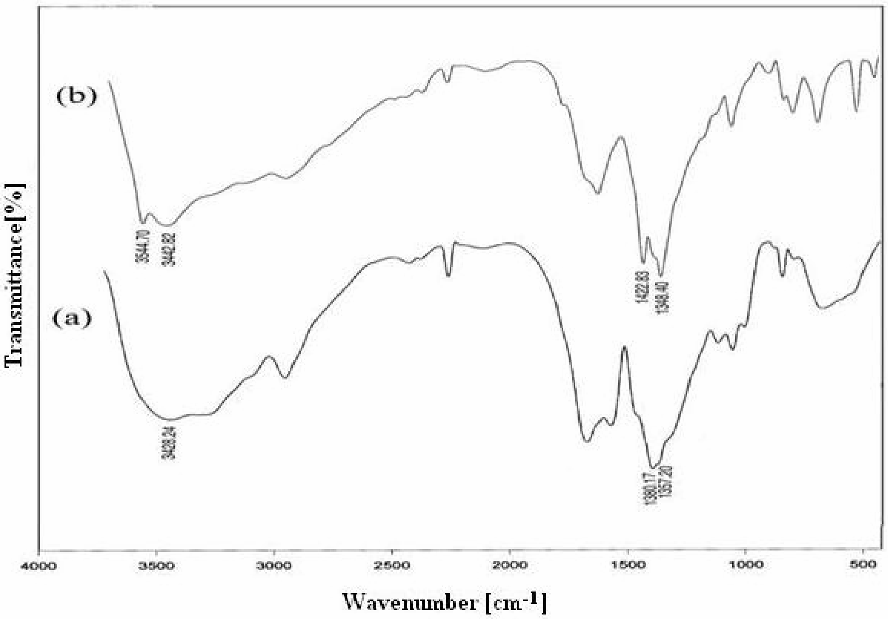


Fig. 2. FT-IR spectra of (a) PAN-DTA50 Cu(II) prepared at pH= 1.5 and (b) PAN-DTA 100 Cu(II) prepared at pH= 4.5.

3.3. Sorption behaviors

The sorption behaviors of Cu(II), Zn(II) and Cd(II) with PAN-DTA50 and PAN-DTA100 resins were determined at various pH. It was found that all metal ions uptake by the resins was increased with increasing pH (Fig. 3.). The highest sorption was observed for Cu(II) which was 2.6 and 5 mmol per gram for PAN-DTA50 and PAN-DTA100 resins at pH 4.5, respectively. On the other hand influence of time on the sorption capacity of the resins for these metal ions was studied and the results are shown in Fig.4. The results indicate that the rate of metal sorption by resins was rapid.

Sorption capacity of the prepared resins for metal ions was compared with already reported functionalized polymers and in the most cases our resins have demonstrated higher sorption values than the reported values [10, 15, 22, 25, 28].

3.4. Recovery of copper and reuse of the resins

The recovery of Cu(II) from PAN-DTA50 and PAN-DTA100 resins was obtained about 95.6% and 83.0%, respectively (Table 2). The reloading of Cu(II) on the PAN-DTA50 and PAN-DTA100 resins was measured, which was found to be about 99.0% and 98.7%, respectively. Thus, it was clear and expectable that prepared chelating resins could be able to reuse for another metal ions.

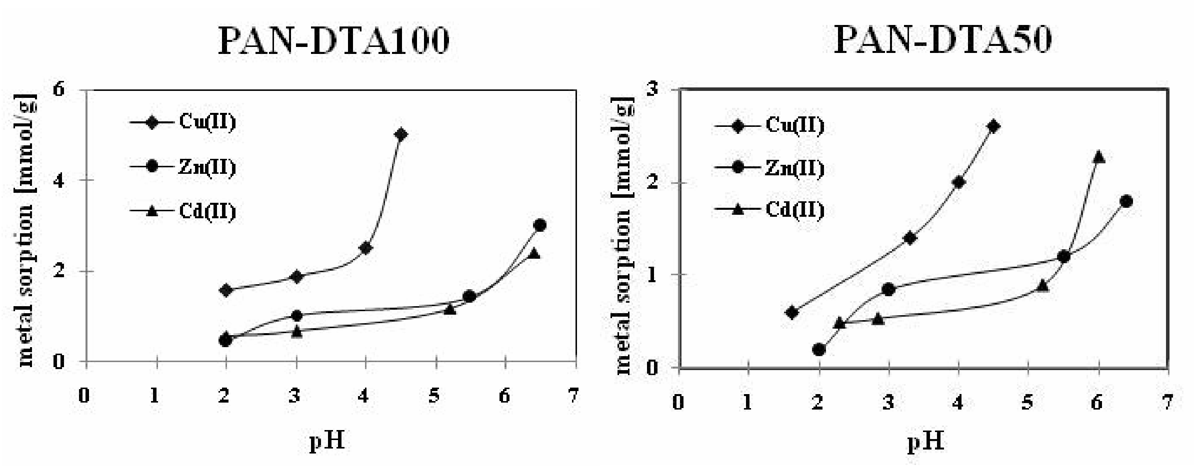


Fig. 3. Effect of pH on metal ions sorption capacities by PAN-DTA resins.

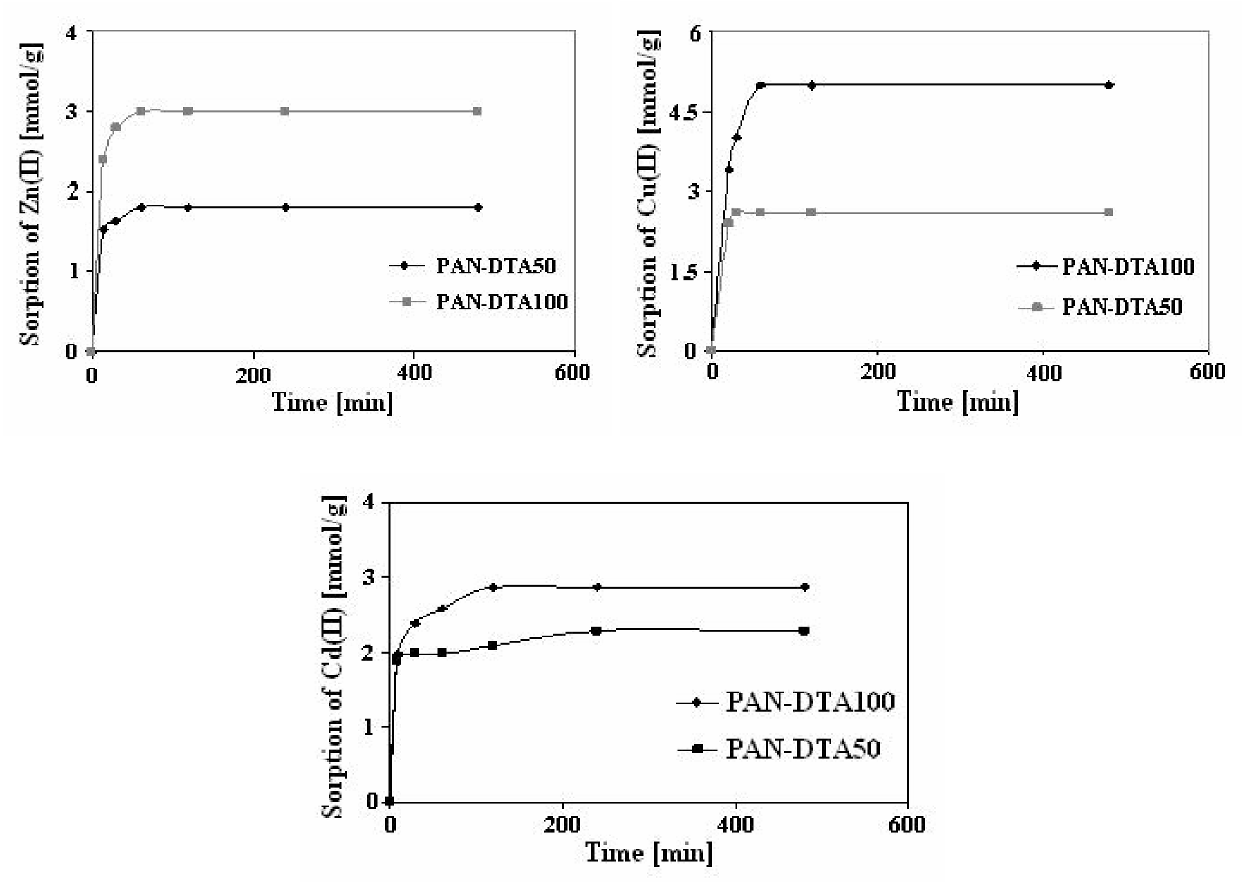


Fig. 4. Sorption rate of Cu(II) at pH= 4.5 (a) Zn(II) at pH= 6.5 (b) and Cd(II) at pH= 6.5 by the PAN-DTA resins.

Table 2
Sorption/desorption of Cu(II) on PAN-DTA resins.

Resins	Sorption (mmol g^{-1})	Desorption mmol g^{-1} (%)	Sorption mmol g^{-1} (%)
PAN-DTA 50	1.90	1.82 (95.6)	1.89 (99.0)
PAN-DTA 100	3.82	3.17 (83.0)	3.77 (98.7)

3.5. SEM analysis

Scanning electron micrographs (SEM) was utilized to study the morphology of the resins and their metal complexes. Fig. 5 shows that there is a drastic difference between morphology of PAN-DTA50 and PAN-DTA100. PAN-DTA50 beads in comparison with PAN [9], does not show considerable change in morphology. Also, there was no distinct morphological difference was noticed between prepared complexes and resins.

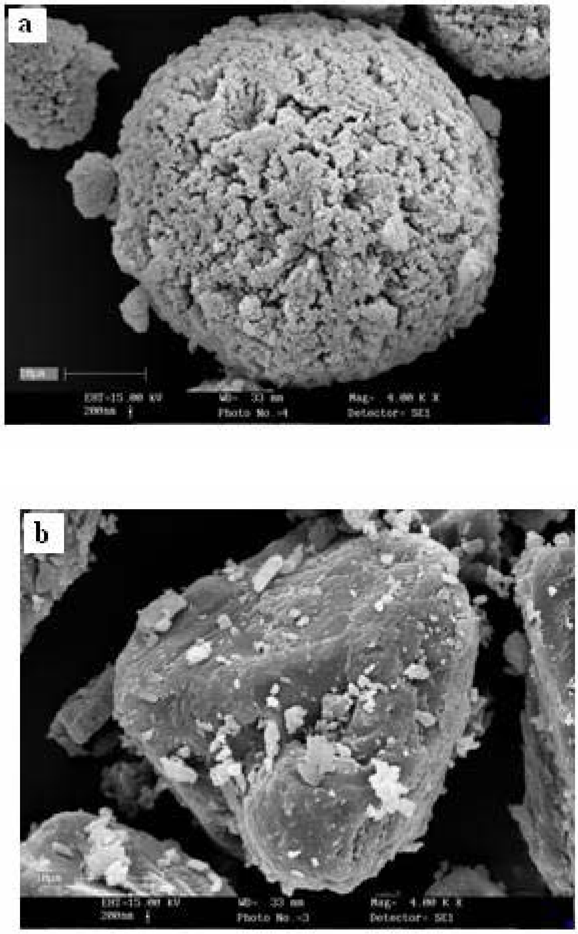


Fig. 5. SEM images of: (a) PAN-DTA50 (×4000) and (b) PAN-DTA100 (×4000).

3.6. Thermogravimetry analysis

The thermal degradation analyses of the prepared resins and their metal complexes were performed with heating rate of 10 ºC per minute in N_2 atmosphere. The TGA of two resins show three steps decomposition with similar pattern. The first stage, ranges between room temperature and 200 ºC for both resins which may be attributed to the loss of adsorbed and bounded water moistures. The second stage of mass loss starts at about 250 ºC and continues up to 375 ºC due to the degradation of grafted functional groups. The last stage begins from 375 ºC up to over 600 ºC which may be attributed to the degradation of the remaining polyacrylonitrile chains (Fig. 6). The TG curves for all metal-resins complexes also show three stages of mass losses. The thermal degradations of copper-resin complexes, prepared at two different pH, are shown in Fig. 7 and 8. The plateau observed at 600 ºC, in which the final remaining mass was over 20-40%, corresponds to the formation of metal oxides. In all cases the resin with more metals has higher residual mass over 600 ºC. These curves also proved that sorption capacity of PAN-DTA100 are more than PAN-DTA50. The thermoanalyses data of resins and their metal complexes are summarized in Table 2.

Table 3
TGA data of resins and their metal complexes.

Resin and complex	tureTemprea (°C)											
	50	100	150	200	250	300	350	400	450	500	550	600
PAN-DTA50	99.8	92.1	88.9	85.6	81.1	74.5	54.5	36.7	21.1	17.8	15.6	13.3
PAN-DTA50 Cu(II) pH=1.6	97.8	92.2	91.1	90.0	85.6	70.0	51.1	38.9	28.9	24.5	22.2	20.0
PAN-DTA50 Cu(II) pH=4.5	98.9	93.3	91.1	90.0	81.1	70.0	62.2	48.9	40.0	37.8	35.6	33.3
PAN-DTA50 Zn(II) pH=6.5	97.8	90.0	88.9	87.8	86.7	77.8	65.6	57.8	52.2	48.9	45.6	42.2
PAN-DTA50 Cd(II) pH=6	98.0	93.1	91.5	90.3	87.5	70.7	45.1	33.9	25.3	23.5	22.3	21.1
PAN-DTA100	97.8	86.7	83.3	81.1	78.9	70.0	47.8	31.1	18.9	15.6	13.3	12.2
PAN-DTA100 Cu(II) pH=2	98.9	95.6	94.5	93.3	91.1	67.8	54.5	47.8	43.3	40.0	38.9	36.7
PAN-DTA100 Cu(II) pH=4.5	98.9	96.7	95.6	94.5	78.9	64.5	60.0	56.7	53.4	51.1	50.0	48.9
PAN-DTA100 Zn(II) pH=6.5	98.9	95.6	94.5	93.3	90.0	77.8	64.5	58.9	54.5	51.1	50.0	48.9
PAN-DTA100 Cd(II) pH=2.9	98.2	96.0	95.5	94.5	93.0	70.8	72.3	41.0	31.5	27.8	26.5	25.0
PAN-DTA100 Cd(II) pH=6.5	98.5	97.0	96.5	94	93.0	80.1	64.5	56.4	53.0	49.0	45.8	44.5

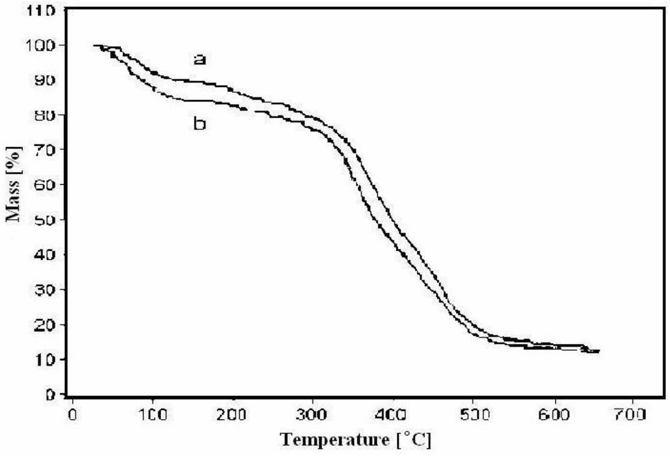


Fig. 6. Thermograms of (a) PAN-DTA50 and (b) PAN-DTA100.

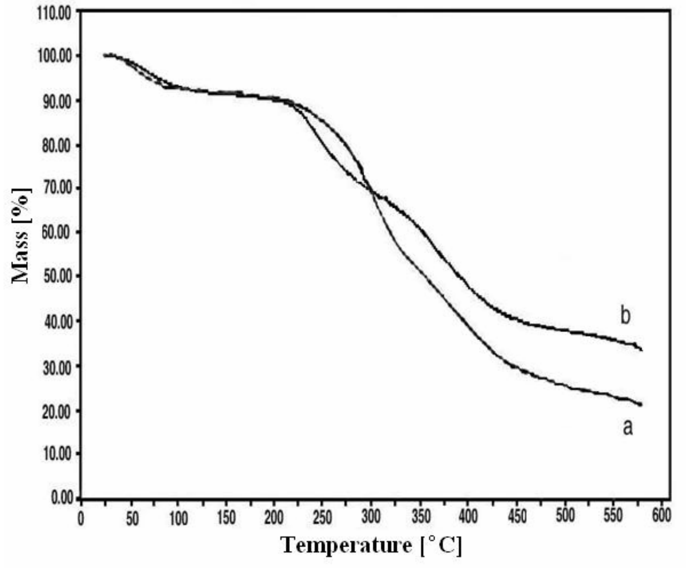


Fig. 7. Thermograms of PAN-DTA50–Cu complexes prepared at pH=1.6 (a) and pH=4.5(b).

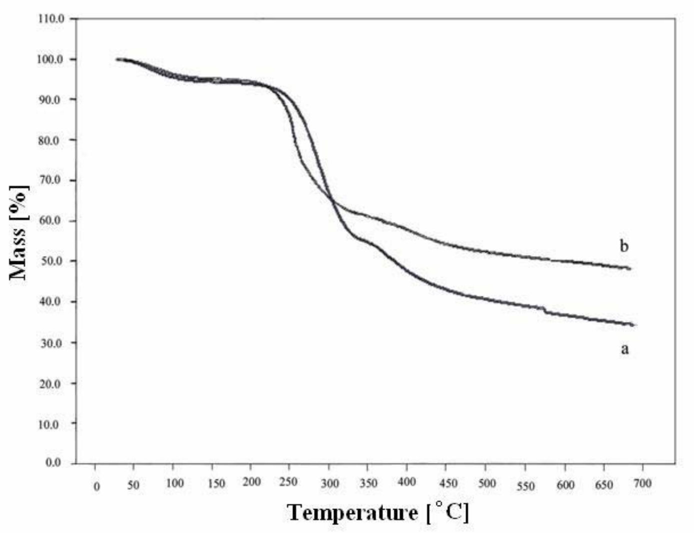


Fig. 8. Thermograms of PAN-DTA100–Cu complexes prepared at pH=2 (a) and pH=4.5 (b).

4. Conclusion

Aminated polyacrylonitrile resins were prepared through the reaction of polyacrylonitrile with various volume percents of diethylenetriamine. The sorption behavior of the resins were studied for Cu(II), Zn(II) and Cd(II) ions and demonstrated that they have acceptable sorption to metal ions in comparing with similar resins. FT-IR spectroscopy study revealed that the amine groups on the resins played an important role in the sorption of Cu(II), Zn(II) and Cd(II) ions from the solution. The SEM micrographs show that there is a drastic difference in morphology of polymer surface when it was modified with pure DTA. The thermogravimetry analysis (TGA) of metal resin complexes showed the presence of metal in final resin complexes.

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