



Removal of Ni(II) From Synthetic Solutions Using New Amine-containing Resins Based on Polyacrylonitrile

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ABSTRACT

Among chelating resins, the amine containing resins which have excellent adsorption property for metal ions are especially applied widely in separation, enrichment, and removing of heavy metal ions. In this paper, new amine containing resins based on polyacrylonitrile (PAN-DTA and PAN-TETA) were prepared through the reactions of polyacrylonitrile with diethylenetriamine (DTA) or triethylenetetramine (TETA) by a rapid, simple, and economically feasible route. The prepared resins which are completely insoluble in water and common organic solvents were used to remove Ni(II) ion from aqueous solutions. The sorption behaviour of the resins for this ion showed that the greater sorption and distribution coefficients (K_d) were obtained at higher pH media. The highest sorptions of Ni(II) on PAN-DTA50, PAN-DTA100, PAN-TETA50 and PAN-TETA100 resins were determined as 1.9, 3.0, 1.8 and 2.9 mmol/g, respectively. It is shown that the amine capacity of the resins is dependent on the volume percentage of DTA or TETA and the maximum capacity of amines obtained are 6.25 and 9.0 mmol/g for PAN-DTA100 and PAN-TETA100, respectively. Also, the recovery of Ni(II) from PAN-TETA50 and PAN-TETA100 resins are estimated about 65% and 61%, respectively. The resins and their metal complexes are studied by FTIR spectroscopy, scanning electronic microscopy (SEM), and thermal gravimetric analysis (TGA). All the analytical methods have confirmed the presence of metal in the metal-resin complexes.

Key Words:

polyacrylonitrile;
diethylenetriamine;
triethylenetetramine;
resin;
metal sorption.

INTRODUCTION

Pollution by toxic heavy metals due to their toxicities in relatively low concentration and tendency to bioaccumulation in the ecosystem, agriculture, and human body has received wide spread attention in recent years. Various approaches such as ion-exchange, reverse osmosis, electrodialysis, precipitation, and adsorption techniques have been developed for the removal and recovery of the metal

ions from sewage and industrial wastewater. Among these techniques, many research works have focused on metal ions removal by sorption on chelating polymers, because they are reusable, easily separable, and with higher adsorption capacities and selectivity having physical and chemical stabilities [1,2].

The use of synthetic resins with various functionalities for chelating

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toxic metal ions by adsorption is a possible method for preventing environmental pollution [3-6]. Polymeric resins are completely insoluble in most aqueous and organic solutions and their stability can be controlled by careful choice of polymer network and type of functional grouping. These resins have received considerable attention in the separation of metal ions owing to their inherent advantages over simple ion-exchange resins, e.g., their higher selectivity for binding heavy metal ions [7-10]. Resins based on polyacrylonitrile are easily prepared and present reactive pendant groups (cyano groups) which can be modified by different types of reagents such as hydroxylamine [11-13], hydrazine [11,13], ethanolamine [11,14], ethylenediamine [14] and thiosemicarbazide [15] through nucleophilic addition and cycloaddition reactions.

Recently, aminated PAN fibres have been also used for removal of metal ions such as chromium, copper, and lead, but with low metal sorption capacity [16,17]. Also, Lin et al. synthesized PAN fibre-supported palladium catalyst which was used in Heck reactions [18].

In this work, new amine-containing resins based on polyacrylonitrile were synthesized through chemical modification of polyacrylonitrile with diethylenetriamine (DTA) and triethylenetetramine (TETA).

Nickel ions represent a serious environmental problem since they are widely used in many industries and general applications. Among them are: industrial effluents, industrial fertilizers, catalysts, gears, magnets, airbag valves, electronics, tooth protects, exhaust smokes, stainless steels, etc. Therefore, in this work we use the obtained resins (PAN-DTA and PAN-TETA) as adsorbents in a series of batch adsorption experiments for the removal of Ni(II) ions from synthetic aqueous solutions. The adsorption behaviours of Ni(II) ions were examined under different solution pH media and contact times. The sorption capacity of the resins for Ni(II) ions was measured by complexometric titration. PAN-DTA and PAN-TETA resins and their nickel (II) complexes were studied by FTIR, scanning electron microscopy (SEM), thermal gravimetry (TG) and elemental analysis.

EXPERIMENTAL

Materials and Instruments

Polyacrylonitrile powder was provided by Polyacryl Co. (Isfahan, Iran) with a molecular weight of $60,000 \text{ g.mol}^{-1}$ (15% acrylic acid based on elemental analysis data). Diethylenetriamine (DTA) and triethylenetetramine (TETA) were purchased from Merck and used without purification. Nickel (II) nitrate $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ was provided by Fluka and used directly. Ethylenediaminetetraacetic acid disodium salt 99% (EDTA-2Na) was provided from Panrak. Murexide was purchased from Merck and used as indicator directly.

The FTIR spectra ($500\text{-}4000 \text{ cm}^{-1}$) were obtained from Unicam 4600 spectrophotometer by using KBr pellets. The SEM 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 (Rate $10^\circ\text{C}/\text{min.}$).

Resins Preparation

Preparation of PAN-DTA50 and PAN-TETA50 Resins

The resins were prepared by adding 5 g of PAN to 50 mL of 50% (v/v in water) diethylenetriamine or triethylenetetramine solution in a 250 mL round-bottom flask. The mixture was stirred on a magnetic stirrer and the reaction was allowed to proceed at $100\text{-}110^\circ\text{C}$ for 29 h. Then, some distilled water was added and the resins were separated from solution by filtration, rinsed with distilled water until the pH of the effluent reached the neutral point, dried at 50°C in an oven overnight, and stored on a desiccator prior to use in the sorption study. The yields of PAN-DTA50 and PAN-TETA50 were 10.5 and 7.76 g, respectively.

Preparation of PAN-DTA100 and PAN-TETA100 Resins

The resins were prepared by adding 2.5 g of PAN to 25 mL of diethylenetriamine or triethylenetetramine in a 100 mL round-bottom flask, and the reaction was carried out at $100\text{-}110^\circ\text{C}$ for 5 h. After completion of the reaction while gelation was occurred, some distilled water was added and the resins were separated from solution by filtration, rinsed with

distilled water until neutrality, dried at 50°C in an oven overnight, and stored in a desiccator prior to use in the sorption study. The yields of PAN-DTA100 and PAN-TETA100 were 4.2 and 5.4 g, respectively.

Sorption of Ni(II) Ions By the Synthesized Resins

Batch sorption experiments were conducted in 50 mL beakers, each of them containing 30 mL of a metal solution prepared with 2 mmol of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (582 mg) in water or HCl solutions with different concentrations to obtain required pH levels. A sample of each resin (0.1 g) was added into each beaker, and the contents in the beakers were stirred by a magnetic stirrer to reach equilibrium conditions and then the pH of the solution was determined to precise point.

After the experiment, the resins were separated from the solutions by filtration, rinsed with aqueous solution of the same pH to remove non-complexed metal ions. Then, the metal-resin complexes were dried at 50°C in an oven. The filtrate solution was collected in a 50 mL volumetric flask and titrated with EDTA-2Na solution in the presence of Murexide indicator.

In investigating the effect of solution pH on the sorption capacity of PAN-DTA and PAN-TETA resins for Ni(II) ion, the sorption time was maintained for 2 h, but the solutions pH levels were changed from 2 to 7.2 for Ni(II). On the other hand, in studying the effect of time on the sorption of these ions, the solution pH was kept at maximum value while the sorption time was changed from 10 min to 8 h.

The distribution coefficients (K_d) of Ni(II) by batch method can be measured for prepared resins. K_d is calculated by the following equation:

$$K_d (\text{mL} / \text{g}) = [\text{Ni}^{2+}]_r / [\text{Ni}^{2+}]_s$$

where, s and r stand for solution phase and resin phase, respectively.

Amine Capacity of the Resins

A sample (about 0.5 g) of the PAN-DTA or PAN-TETA resin was completely converted to a H^+ form by treating with excess solution of 0.1 M HCl in a beaker for 4 h. The resin was separated from the acidic solution by filtration, rinsed with distilled water until its pH reached the neutral point and finally it was

dried at 50°C to a constant weight. An exact amount of 0.2 g of the H^+ form of resin was weighed into a 250 mL Erlenmeyer flask and 25 mL of standard 0.1 M NaOH solution was added to the flask equipped with a stopper and was shaken for about 4 h. After shaking, a 10-mL aliquot of the supernatant solution was back-titrated to the phenolphthalein end point with standard 0.1 M HCl solution.

Recovery of Ni(II) and Reuse of Resins

Exactly 150 mg of each resin containing nickel was weighed into a 100 mL beaker and 30 mL of 4 M hydrochloric acid was added into the beaker and the mixture was shaken for 2 h. Then, the resin was separated from solution by filtration, eluted with 30 mL of 12.5% aqueous ammonia, washed with distilled water until the neutral point was reached and it was finally dried at 50°C to a constant weight. The resin was used again for the sorption of nickel ions.

RESULTS AND DISCUSSION

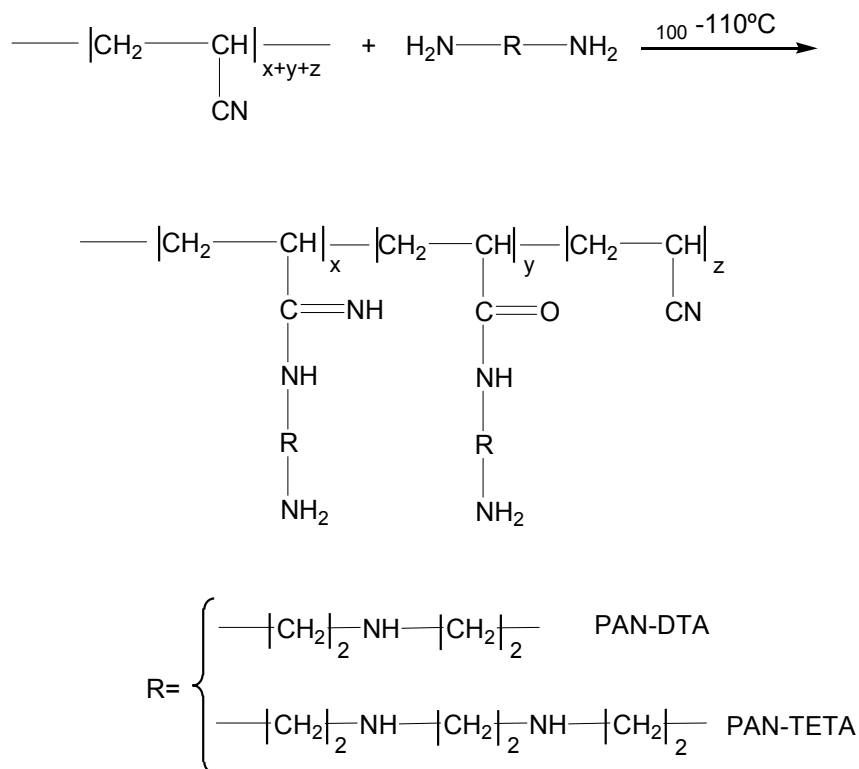
As shown in Scheme I, two new amine-containing resins, i.e., PAN-DTA and PAN-TETA were synthesized through reactions between polyacrylonitrile (PAN) powder and diethylenetriamine (DTA) or triethylenetetramine (TETA).

The resins were prepared by a modified route according to Deng et al. [17] and Lin et al. [18] works as they used modified PAN fibres. The ability of the prepared resins in powder form to remove metal ions is higher than that of the functionalized fibres e.g., to remove Cu (II) [19]. The prepared resins are completely insoluble in water and common organic solvents such as acetone, methanol, chloroform, and DMSO.

The introduced amine groups into PAN structure are suitable sites to coordinate with various metal ions such as Ni(II).

FTIR Spectra of the Resins

According to FTIR spectra, after reaction of the PAN with 50 and 100 volume percentages of DTA or TETA, the spectra of the obtained amine containing resins show many significant changes. The strong broad band ranging from 3200-3500 cm^{-1} usually



Scheme I. Synthesis of PAN-DTA and PAN-TETA resins.

corresponds to the combination of the stretching vibration bands of both OH and NH groups (Figures 1 and 2).

On the other hand, a significant reduction in the peak absorption of C≡N groups of the PAN at about 2245 cm⁻¹ was observed by increasing the volume percentages of DTA or TETA. The peak of C≡N stretching has not disappeared completely, which suggests that only part of the nitrile groups on the PAN were converted during the treatment. In addition, the new bands at 1655, 1561, and 1392 cm⁻¹ for PAN-DTA50 and PAN-TETA50 and also 1648, 1598, and 1448 cm⁻¹ for PAN-DTA100 and PAN-TETA100 resins suggest that the amide and amine groups were introduced into the resins.

Figures 1 and 2 also show the FTIR spectra of the prepared resin-metal complexes. By comparing curves (a) and (b) and curves (c) and (d), it is observed that the peak of N-H stretching moved towards higher wavenumber after adsorbing Ni(II) ion by the resins. Meanwhile, the peak of C-N bending moved towards lower wavenumber. All these

displacements occurred because of the combination of nitrogen atoms in N-H and =N-H, and of oxygen atom in O=C-N with Ni(II) ions to form chelate complexes.

Sorption Behaviour

The binding properties of nickel ions with PAN-DTA50, PAN-DTA100, PAN-TETA50, and PAN-TETA100 resins were determined at various pH levels. It was found that Ni(II) uptake by the resins is increased with increasing pH (Figure 3).

The sorption values of Ni(II) by PAN-DTA and PAN-TETA resins and its distribution coefficient at relative pHs are given in Table 1. In all cases, the sorptions of Ni(II) ions by PAN-DTA100 and PAN-TETA100 resins are more than those of PAN-DTA50 and PAN-TETA50 resins due to their high amine contents. According to Table 1 and Figure 3 the highest sorption of Ni(II) ions on PAN-DTA50, PAN-DTA100, PAN-TETA50, and PAN-TETA100 resins were 1.9, 3.0, 1.8 and 2.9 mmol/g, respectively. Also, Table 1 summarizes the distribution coefficients (K_d)

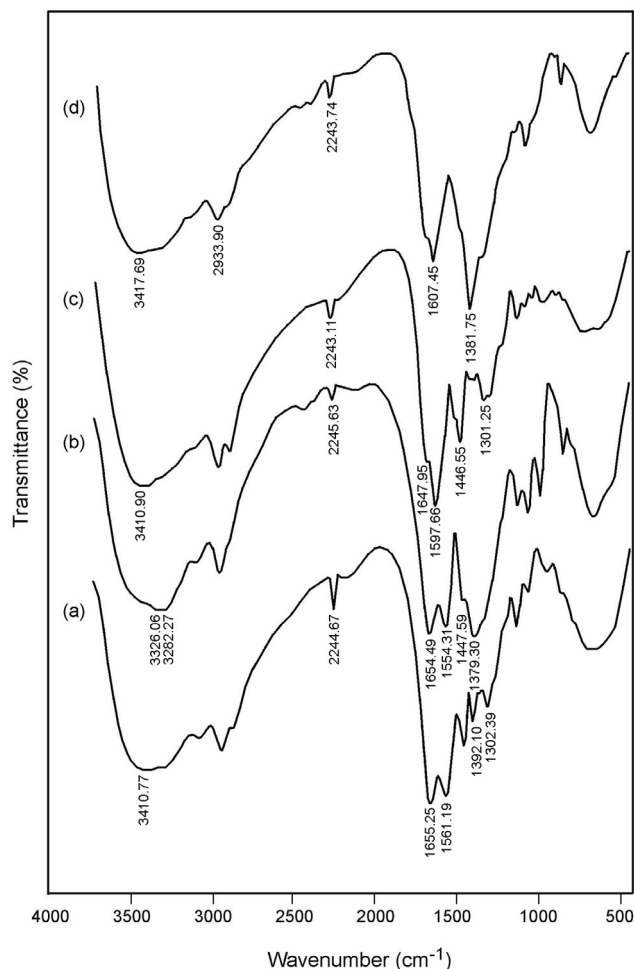


Figure 1. FTIR spectra of: (a) PAN-DTA50, (b) PAN-DTA50-Ni(II), (c) PAN-DTA100, and (d) PAN-DTA100-Ni(II).

of Ni(II) ion for each of the prepared resins. The PAN-DTA100 and PAN-TETA100 resins have the highest K_d for Ni(II) ions at pHs 2 and 5, respectively.

On the other hand, influence of time on the

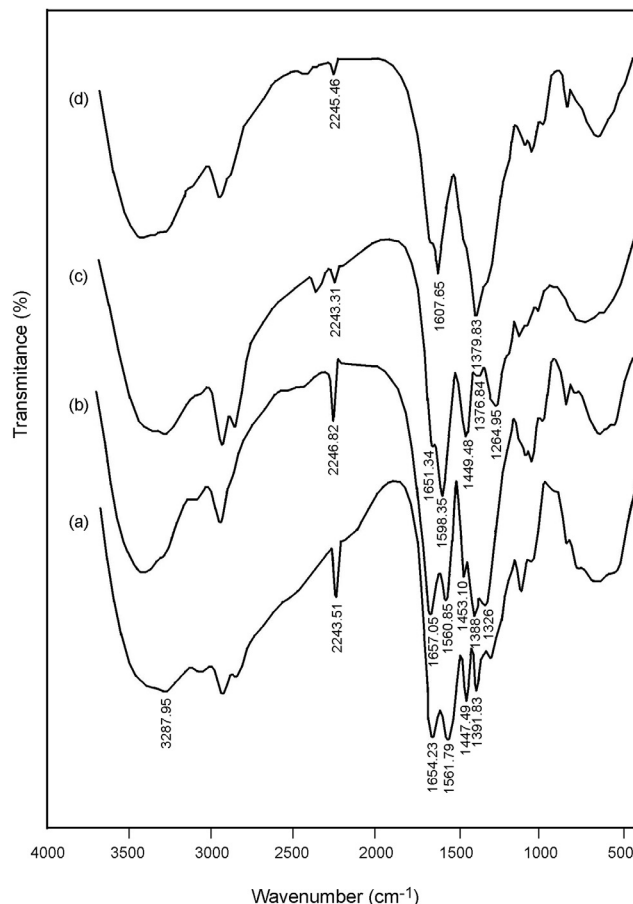


Figure 2. FTIR spectra of: (a) PAN-TETA50, (b) PAN-TETA50-Ni(II), (c) PAN-TETA100, and (d) PAN-TETA100-Ni(II).

sorption capacity of the resins for nickel ions was studied (Figure 4).

According to these data, the rate of nickel sorption by resins was rapid and then reached a constant value after about 1 h. Sorption capacity of the prepared resins for Ni(II) ions was compared to other

Table 1. Sorption of Ni(II) by PAN-DTA and PAN-TETA resins and its distribution coefficient at different pH values.

Resins	Ni(II) sorption at maximum pH		Ni(II) sorption at pH = 2		Ni(II) sorption at pH = 5	
	Sorption capacity (mmol/g)	K_d (mL/g)	Sorption capacity (mmol/g)	K_d (mL/g)	Sorption capacity (mmol/g)	K_d (mL/g)
PAN-DTA50	1.9 (pH=6.4)	31.51	0.60	9.27	1.44	23.26
PAN-DTA100	3.0 (pH=7.2)	52.91	0.90	14.13	1.80	29.65
PAN-TETA50	1.8 (pH=5)	29.65	0.65	10.08	1.80	29.65
PAN-TETA100	2.9 (pH=7)	50.88	0.70	10.89	1.88	31.13

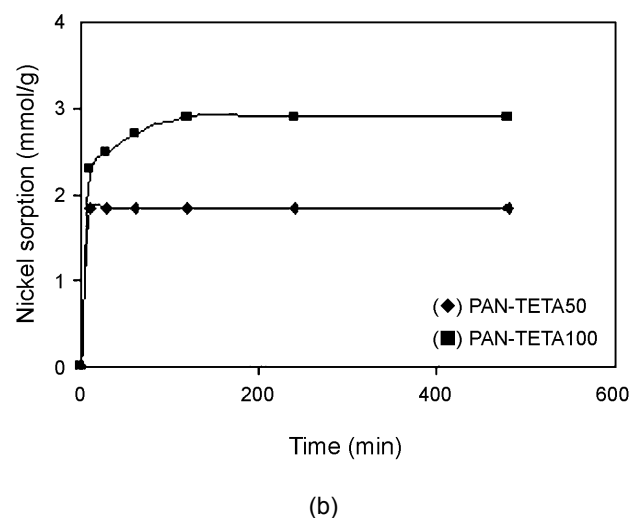
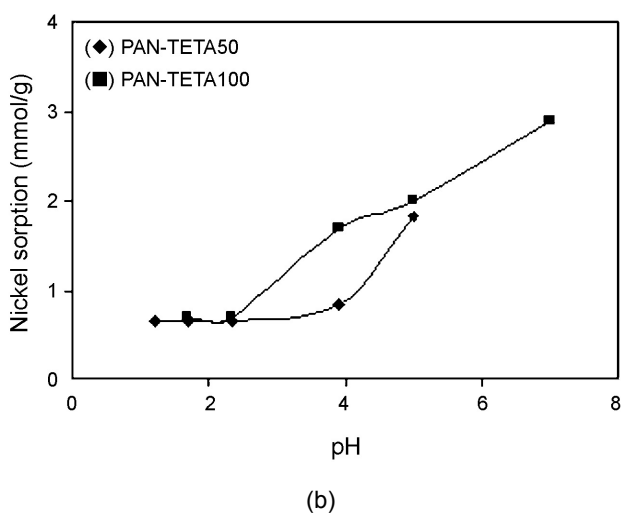
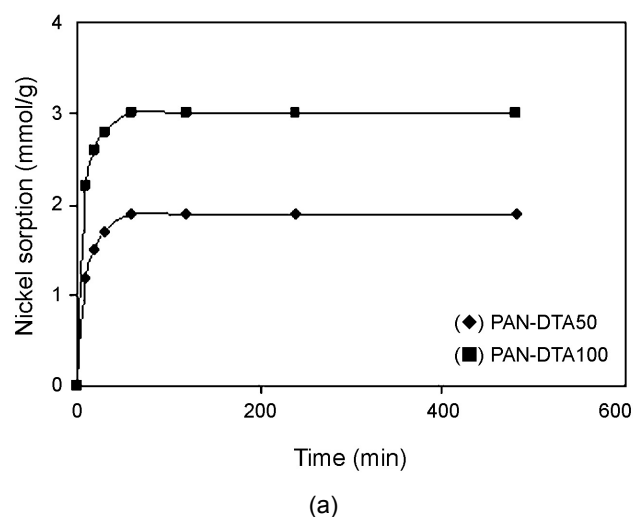
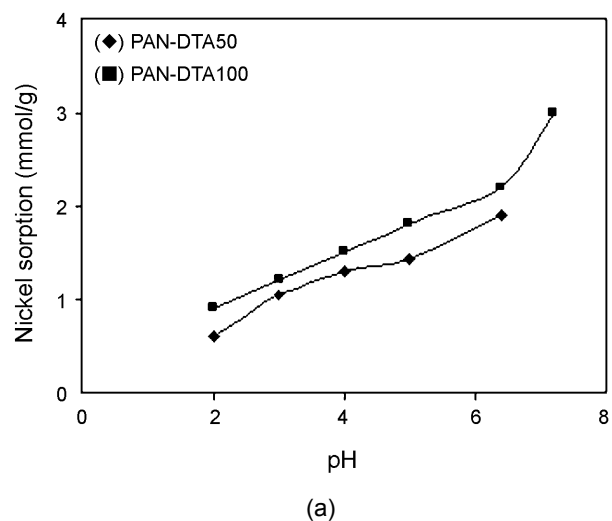


Figure 3. Effect of pH on Ni(II) sorption by: (a) PAN-DTA and (b) PAN-TETA resins.

Figure 4. Sorption rate of Ni(II) by: (a) PAN-DTA and (b) PAN-TETA resins.

functionalized polymers and in most cases our resins have demonstrated higher sorption values [11,13,14, 20-23].

Amine Capacity of the Resins

The nitrogen content and amine capacity of the resins were increased with increasing volume percentage of DTA or TETA (Table 2). The maximum capacity of amine was obtained approximately as 6.25 mmol. g⁻¹ for PAN-DTA100 and 9.0 mmol. g⁻¹ for PAN-TETA100.

Desorption Studies

The recovery of Ni(II) from PAN-TETA50 and PAN-TETA100 resins was performed according to the

method explained above and estimated for each as ~65% and ~61%, respectively. The separate reloading of Ni(II) on PAN-TETA50 and PAN-TETA100 resins was performed and it is shown that both chelating resins have enough ability to be reused (Table 3).

Table 2. Nitrogen content and amine capacity of the synthesized resins.

Resin	Amine capacity* (mmol/g)	Total Nitrogen** (mmol/g)
PAN-DTA50	4.70	14.2
PAN-DTA100	6.25	16.6
PAN-TETA50	5.90	13.9
PAN-TETA100	9.00	16.2

(*) results from back titration; (**) results from elemental analysis.

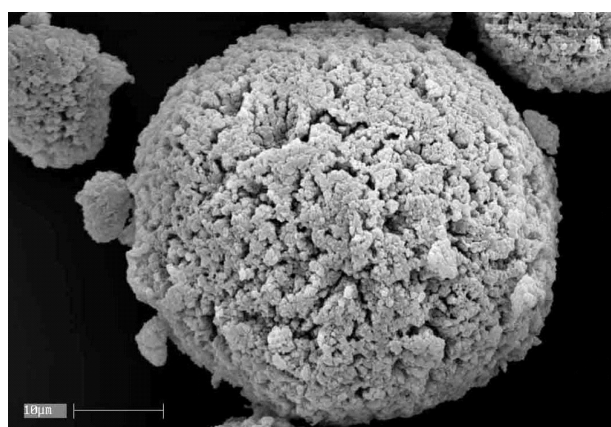
Table 3. Adsorption/desorption of Ni(II) ions by PAN-TETA resins using HCl 4M as desorbent.

Resin	Sorption (mmol/g)	Desorption (mmol/g)
PAN-TETA50	1.4	0.9 (65)
PAN-TETA100	2.5	1.5 (60.8)
PAN-DTA100	3.0	1.9 (62.8)

SEM Analysis

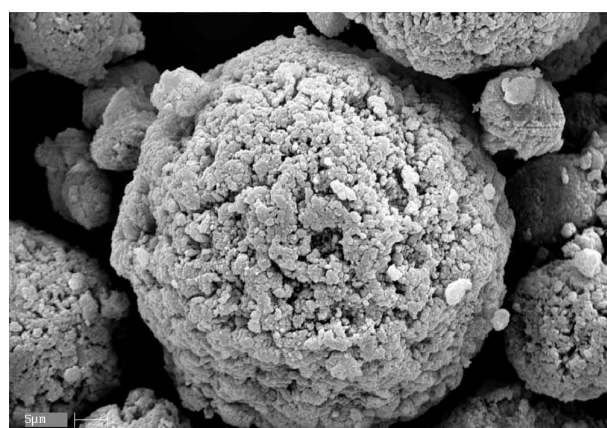
Scanning electron microscopy (SEM), in $\times 3000$ and $\times 4000$ magnifications, was utilized to study the resins and their metal complex morphologies. Figure 5 shows that except PAN-DTA100, there is not any

drastic difference among morphologies of the resins and that of the unmodified PAN [14]. The reason is that the presence of water in preparing PAN-DTA50 and PAN-TETA50 does not allow much reaction between PAN and DTA or TETA. However, the reaction between PAN and DTA in preparing PAN-DTA100, due to the absence of water, is stronger and therefore some morphological changes are observed. But because of high viscosity of TETA in preparation of PAN-TETA100 we did not observe any change in its morphology. Also, the SEM micrographs of resins after nickel sorption (resin-metal complexes) did not show any morphological difference compared with the initial resins.



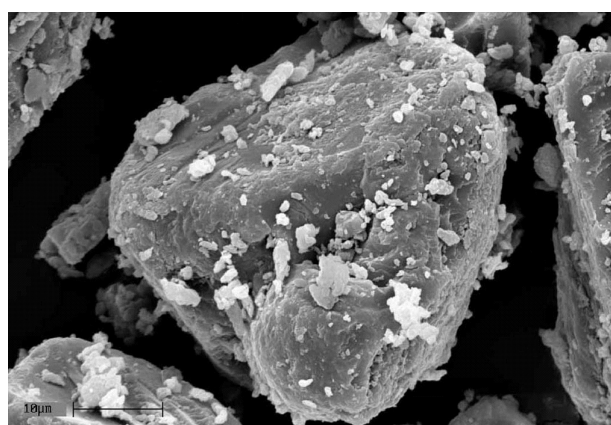
10 μ m

(a)



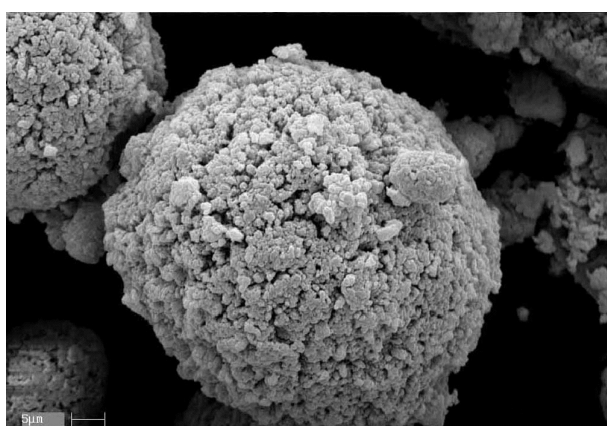
5 μ m

(c)



10 μ m

(b)



5 μ m

(d)

Figure 5. SEM images of: (a) PAN-DTA50 ($\times 4000$), (b) PAN-DTA100 ($\times 4000$), (c) PAN-TETA50 ($\times 3000$), and (d) PAN-TETA100 ($\times 3000$).

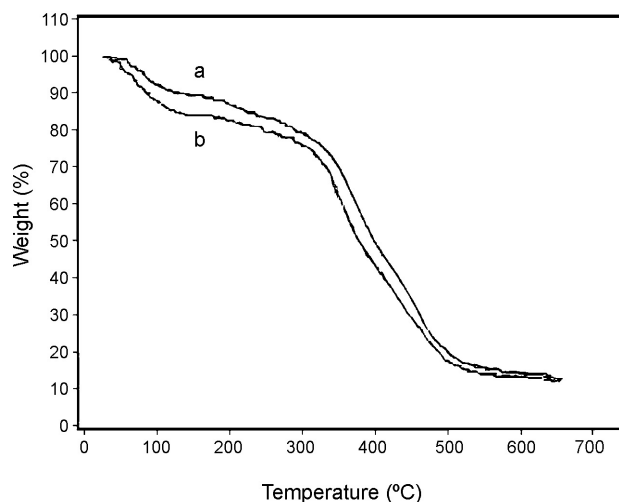


Figure 6. Thermograms of: (a) PAN-DTA50 and (b) PAN-DTA100.

Thermogravimetry Analysis

The thermal degradation analyses of the prepared resins and their metal complexes were performed with heating rate of $10^{\circ}\text{C min}^{-1}$ in an N_2 atmosphere (Figures 6-9). The TGA of resins shows a weight loss of the same pattern at three stages for all resins. The first stage ranges between room temperature and 200°C for all resins which may be attributed to the loss of adsorbed and bound water. The second stage of weight loss starts at about 250°C and continues up to 375°C due to the degradation of grafted functional groups. The last stage begins from 375°C up to over

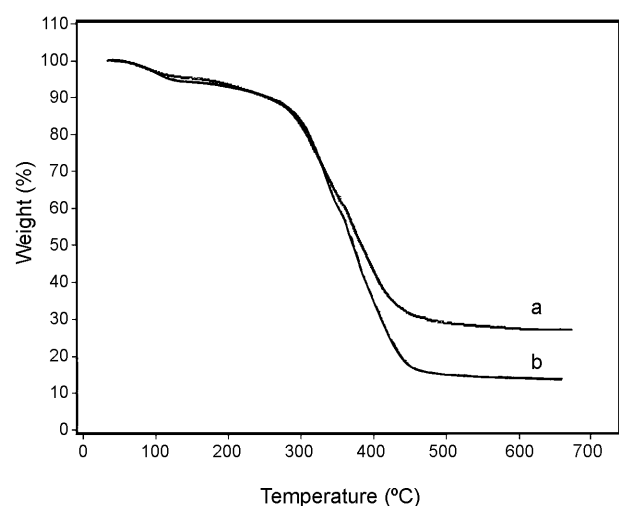


Figure 7. Thermograms of: (a) PAN-TETA50 and (b) PAN-TETA100.

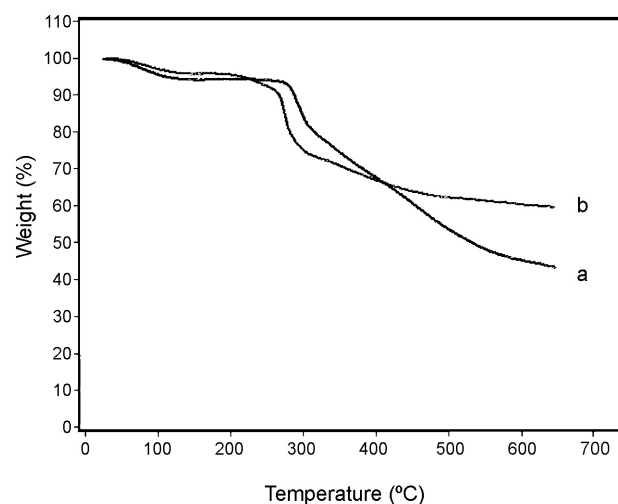


Figure 8. Thermograms of: (a) PAN-DTA50-Ni(II) (pH 6.4) and (b) PAN-DTA100-Ni(II) (pH 7.2).

550°C which may be due to degradation of the remainder of polyacrylonitrile chains.

The thermal degradations of metal-resin complexes prepared at maximum pH are shown in Figures 8 and 9. The TGA curves for all metal resins also show three stages of weight loss. The plateau observed above 600°C , in which the final remaining weight was over 40%, corresponds to the formation of metal oxides. In all cases the resin with more metals has higher residual mass over 600°C . These curves also prove that sorption capacity of PAN-DTA100 and PAN-TETA100 is more than PAN-DTA50 and PAN-TETA50.

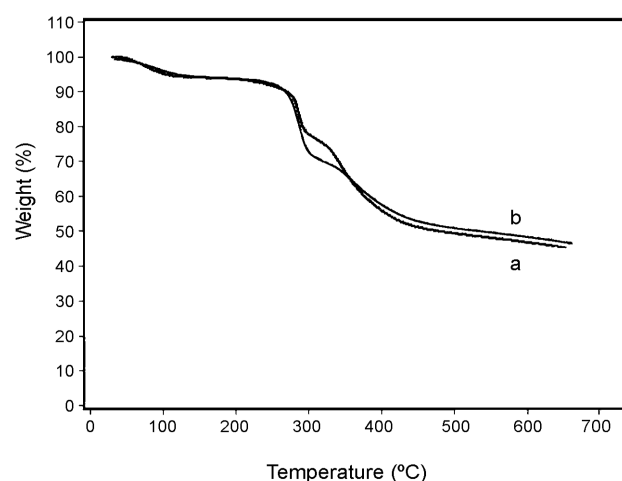


Figure 9. Thermograms of: (a) PAN-TETA50-Ni(II) (pH 5), and (b) PAN-TETA100-Ni(II) (pH 7.2).

CONCLUSION

Aminated polyacrylonitrile resins were prepared through the reaction of polyacrylonitrile powder with 2 volume percentages of diethylenetriamine and triethylenetetramine (50 and 100). The sorption behaviour of the resins was studied for Ni(II) ion and showed that the resins have acceptable sorption to Ni(II) ions compared to similar resins. FTIR spectroscopy, elemental analysis, thermal gravimetry analysis (TGA) and amine determination proved the formation of amine-containing resins. TGA and FTIR spectroscopy studies on metal-resin complexes showed the presence of Ni(II) ions in the final metal-resin complexes. The SEM micrographs showed that there is not any drastic difference in the morphology of resins compared with unmodified PAN, except PAN-DTA100.

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