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Modification and Characterization of Polyacrylonitrile Fiber by Chelating Ligand for Preconcentration and Determination of Neodymium Ion in Biological and Environmental Samples

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ABSTRACT: In this study a chelating fiber containing iminodiacetic acid was prepared via the stepwise modification of acrylic fibers, polyacrylonitrile. The resulting modified fiber has been characterized by Fourier transform infrared spectroscopy, elemental analysis, thermogravimetric analysis, and scanning electron microscopy. Then polyacrylonitrile- iminodiacetic acid was applied for preconcentration and determination of trace Nd(III) ion from human biological fluid and environmental water samples with inductively coupled plasma – atomic emission spectroscopy. The optimum pH value for sorption of the metal ion was 6. The sorption capacity of functionalized resin is 8.9 mg g^{-1}. A recovery of 100% was obtained with preconcentration factor 10 for the Nd(III) with 0.5 M nitric acid as eluting agent. The profile of Nd(III) uptake on this sorbent reflects good accessibility of the chelating sites in the modified polyacrylonitrile. Scatchard analysis revealed that the homogeneous binding sites were formed in the polymers. The equilibrium adsorption data of Nd(III) on modified fiber were analyzed by Langmuir models. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

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INTRODUCTION

The modification of polymers has received much attention in recent years. Among different types of polymer adsorbent, polymer fibers have attracted great interest in recent years.[1] This can be related to their structure and characteristics, like high specific surface, small cross-section, uniformity in diameter (in macroscopic scale), and long length of fiber to diameter.[2] Among synthetic fibers, acrylic fibers seem to be important fibers because of their potential applications in many industries.[3] The adsorbent polyacrylonitrile (PAN) fibers are efficient materials in separation and removal of metal ions especially from diluted solutions.[4–6] These proclaimed advantages are mainly attributed to fibers, high adsorption capacities, fast adsorption equilibrium, high recycling rate, and low production cost. Furthermore, it is known that PAN fiber has good chemical resistance, thermal stability, low flammability, and very good mechanical properties.[7,8] Moreover, PAN fiber is a good substrate for the modification due to its functional group. In recent decades, special attention has been paid to modification for accessing to higher adsorption capacities, fast adsorption equilibrium, and better chemical and physical properties.

Neodymium (Nd) is a rare earth element. Rare earth, a kind of natural mineral, has been used as the beneficial elements to crops for quite a long time. Rare earth has been found to have some controlling effects on many plant diseases. The Nd found in the ocean is lithogenic (i.e., derived from the lithosphere, including continental shelf and slope sediments supplied by erosion).[9] It is brought to the ocean in dissolved or particulate phases by rivers, the atmosphere or remobilization from margin sediments. Within the ocean, most of the Nd is found in the dissolved phase; the particulate phase represents only 5%–10% of the total content.[10] The direct determination of trace elements such as neodymium in real samples is a difficult task. The main restrictions come from the complexity of the matrix and the extremely low concentration's of analytes in those samples which are often below the detection limits of available

techniques.[11,12] Preconcentration is a very important issue for achievement of low detection limits.[13–16]

The purpose of this study is to indicate the feasibility of modification of PAN fiber with chelating ligand, iminodiacetic acid and using this modified fiber as a solid-phase extractant for preconcentration of trace neodymium in biological fluid and environmental water samples. Trace neodymium can be retained on the surface of modified PAN fiber and then desorbed with 0.5 M nitric acid prior to determination by inductively coupled plasma – atomic emission spectroscopy. This proposed novel method has advantages of good accuracy and precision, high recovery, and preconcentration factor.

EXPERIMENTAL

Reagents and Solutions

Polyacrylonitrile (PAN) fibers, consisting of 93.5% (w) acrylonitrile and 6.5% (w) methylacrylate, were purchased from Iran Polyacryl, Isfahan, Iran. Raw acrylic fibers used in this study were cut, washed with methylene chloride and distilled water and air-dried. All chemicals consisting of $Pb(NO_3)_2$, $SnCl_2.2H_2O$, $Co(NO_3)_2.6H_2O$, $MnSo_4.H_2O$, $HgCl_2$, $MgCl_2.6H_2O$, $Ni(NO_3)_2.6H_2O$, $CuSO_4.5H_2O$, $Nd(NO_3)_2$, HNO_3, NaOH, iminodiacetic acid (IDA), Thionyl chloride were obtained from Merck (Darmstadt, Germany).

The stock solution (500 mg L^{-1}) of Nd(III) were prepared by dissolving appropriate amounts of $Nd(NO_3)_2$, in deionized water. To adjust the pH of the solution, 0.01 M acetic acid–acetate buffer (pH 3–6.5) or 0.01 M phosphate buffer (pH 6.5–9) were used.

Instruments

Inductively coupled plasma – atomic emission spectroscopy (ICP-AES) Varian, Vista-pro (Salt lake city, Australia) was used for measuring Nd(III) in solution. The pH measurements were made with a Metrohm model 744 pH meter (Zofingen, Switzerland). Fourier transform infrared spectroscopy (FTIR) was recorded by FT-IR-410, Jasco, Easton, Maryland. Thermogravimetric analysis (TGA) was carried out using a TGA-50H (Shimadzu Corporation). The samples were heated at the rate of 10°C/min under inert Argon gas condition, between 25°C to 800°C. Micrograph of the fibers before and after modification was taken using scanning electron microscopy (Varian Australia Vista Pro).

Chemical Modification of PAN fiber with IDA

The modification of PAN fiber was carried out with three steps as follows:

- Step 1: 1.5 mL absolute ethanol was added in a round-bottomed flask fitted with a reflux condenser. The flask was cooled in ice and 0.5 mL of concentrated sulfuric acid was added slowly with frequent shaking. 1.5 g of fiber was added to the flask, and then the solution was stirred at 90°C in a water bath for 15 h. The hydrolyzed polyacrylonitrile fibers were collected, rinsed with deionized water, and then air-dried.
- Step 2: The hydrolyzed of PAN fibers (0.1 g) was added in flask containing 5 mL thionyl chloride with a reflux condenser connected at the top. The solution was refluxed at 65°C in a water bath for 6 h. The modified polyacrylonitrile fibers were collected, rinsed with methanol, deionized water, and then air-dried.
- Step 3: The final modified PAN containing chelating ligand was prepared by adding 0.1 g of modified fiber from step 2 to 10 mL of 1 M IDA solution. The solution was stirred at room temperature for 4 h. The modified polyacrylonitrile fiber (PAN-IDA) were rinsed with deionized water until neutrality was reached, and then it was dried in an air and collected in a desiccator prior to use for further study. The methodology used to synthesize modified PAN is summarized in Figure 1.

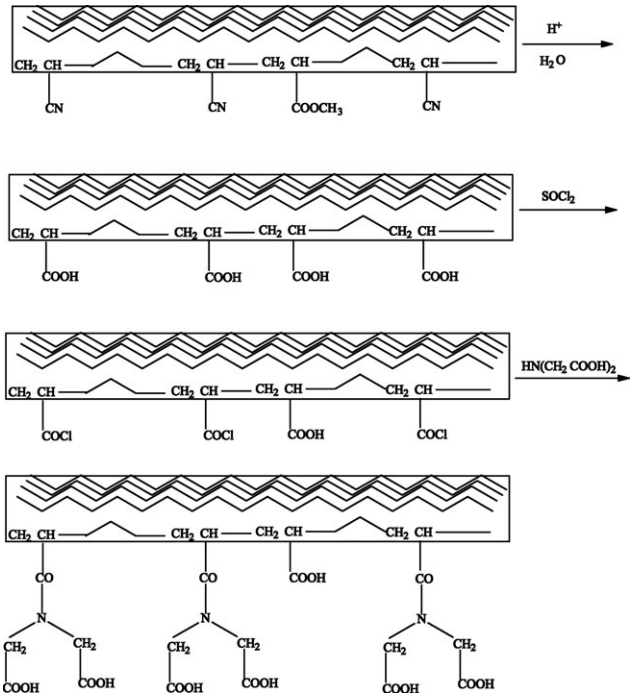

Figure 1. Schematic representation of the methods of polymer modification.

Batch Method of Nd(III) Adsorption

A sample solution (50 mL) containing (0.5 μg mL^{-1}) of Nd(III) was taken in a glass stopperd bottle, and the pH was adjusted to optimum value (6). The 0.1 g of PAN-IDA fiber was put in oven (100°C) for an hour and added to the bottle and the mixture was shaken for optimum time. The resin was taken out and sorbed Nd(III) was eluted with 0.5 M nitric acid (5 mL). The concentration of the metal ion in the eluent was determined by ICP-AES.

Isotherm Studies

Isotherm studies were carried out by adding a fixed amount of adsorbent (0.1 g) to a series of beakers filled with 50 mL diluted solutions of Nd(III) (10–100 μg mL^{-1}). The beakers were then sealed and placed in a water bath shaker and shaken at 300 rpm for 4 h at 20°C and pH 6. pH adjustments have been done using 0.01 M acetate buffer. The beakers were then removed from the shaker, and the final concentration of Nd(III) in the

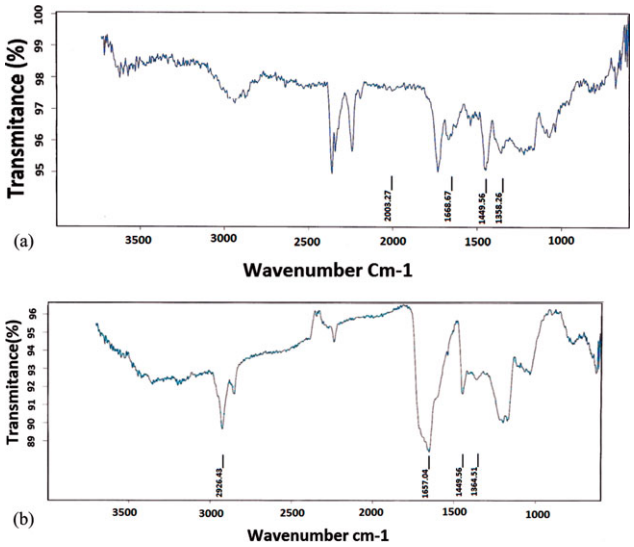

Figure 2. FTIR Spectra of (a) PAN, (b) PAN-IDA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

solution was measured by ICP-AES. The amount of Nd(III) at equilibrium q_e (mg g^{-1}) on PAN-IDA fiber was calculated from the following equation:

$$q_e = (C_0 - C_e)\mathrm{V/W} \quad (1)$$

where C_0 and C_e (mg L^{-1}) are the liquid phase concentrations of Nd(III) at initial and equilibrium, respectively, V (L) the volume of the solution and W (g) is the mass of PAN-IDA used.

RESULT AND DISCUSSION

Characterization of Modified PAN

FTIR Spectrum. The IR spectra of PAN fibers before and after modification are shown in Figure 2. This Figure indicated the related peak to CN (2244 cm^{-1}) was disappeared in modified PAN, that means CN groups in the modified fibers are diminished and confirmed the modification.

Elemental Analysis

The instruction used in this study is reported in Thermofinnigan elemental analyzer manual. Elements of C, H, and N in the sample and standards in a column containing oxidant at 900°C were converted to CO_2, H_2O, and N_2, respectively. They were separated in a GC column containing molecular sieve and detected by a thermal conductivity detector. The percentages of C, H and N in the sample were ascertained after drawing the calibration curve for standards and data processing for the sample.

The data of elemental analysis of row PAN and modified PAN, are listed in Table I. This Table demonstrated that the percentage of nitrogen in modified PAN was lower than the unmodified PAN. This is due to conversion of C≡N groups to C—N$(CH_2COOH)_2$.

Thermogravimetry Analysis

TGA of the row PAN shows two-step weight loss up to 800°C. The weight loss up to 100°C was due to the water molecules in the fiber. The row fiber is stable up to 300°C. The major weight loss after 320°C is due to decomposition of the polymer fiber. The modified PAN shows different thermal behavior. The weight loss up to 100°C was due to the water molecules in the polymer fiber and the weight loss 200–320 was due to the dissociation of chemically immobilized moiety and the polymeric matrix (Figure 3). The major weight loss after 320°C is due to decomposition of the PAN-IDA.

Table I. The Data of Elemental Analysis of PAN and PAN-IDA Fiber

	Weight (%)		
Sample	C	H	N
PAN	65.5	5.72	23.55
Modified PAN	55.7	5.76	15.28

Surface Morphology of the Row and Modified Fibers

Scanning electron microscopy (SEM) was used to examine the external surface of the row and modified PAN fiber. The SEM images are presented in Figure 4. The surface of unmodified PAN has a smooth and highly homogeneous appearance. As shown in Figure 4, in comparison with the surface of the PAN-IDA, surface of raw PAN were less coarse and groovy because PAN-IDA fiber have grafted chelating ligand.

Nd(III) Sorption Parameters

The degree of metal sorption at different pH values was determined by the batch equilibration technique.[17,18] The optimum pH values for quantitative uptake of metal ions were ascertained by measuring the Nd(III) content in supernatant liquid and eluent by ICP-AES. The eluent was obtained by desorbing the metal ion from modified PAN with 0.5 M nitric acid (10 mL). The optimum pH range for the sorption of the metal ion is shown in Figure 5. The maximum recovery was 100% at pH 6. At very low pH (e.g., pH 3.5) the PAN-IDA fiber surface has high positive net charge and therefore, adsorption sites are less favorable for Nd(III) and thus, the adsorption amount is small. At alkaline pH Nd(III) can precipitate with OH^- in the solution.

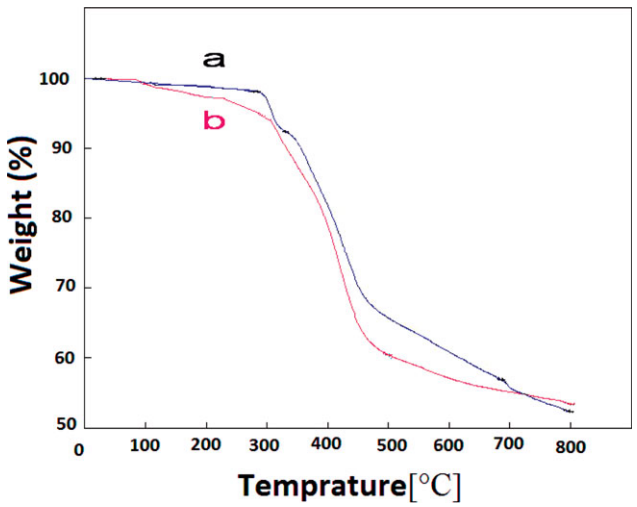

Figure 3. Thermogravimetry analysis of row PAN (a) and PAN-IDA (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

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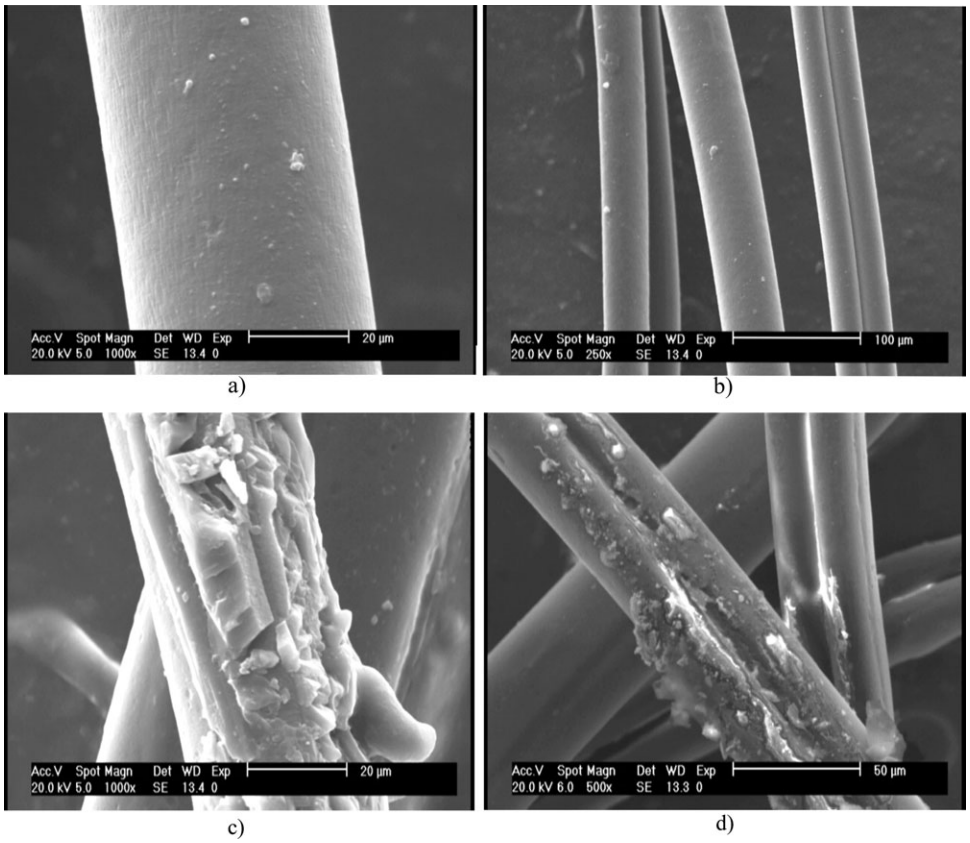

Figure 4. SEM photograph of row PAN fibers (a and b) and modified PAN (c and d).

The saturated adsorption capacity of the PAN-IDA was shown in Figure 6. This figure indicates the effect of initial concentration of the Nd(III) in the solution on sorption capacity of Nd(III) by modified PAN. The capacity increased with increasing initial concentration of the Nd(III) in the solution (9.2 mg g^{-1}).

Sorption of Nd(III) by PAN-IDA fiber was studied at different length of time (2–120 min) under optimum pH (6). The sorption as a function of contact time for Nd(III) is shown in Figure 7. Less than 30 min shaking was required for about 86% sorption. The profile of Nd(III) uptake on this sorbent reflects good accessibility of the chelating sites in the PAN-IDA fiber.

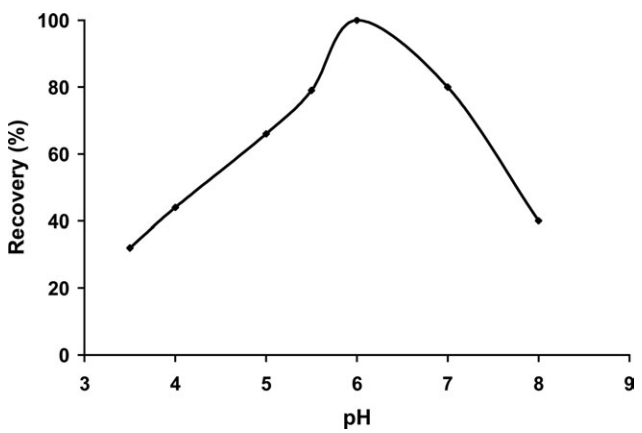

Figure 5. Effect of pH sorption of Nd(III) onto PAN-IDA.

The equilibrium data were correlated by Langmuir for Nd(III) adsorption on PAN-IDA fiber. Langmuir treatment is based on the assumption that maximum adsorption corresponds to a saturated monolayer of adsorbate molecule on the adsorbent surface, with a constant energy of adsorption and no transmigration of adsorbate in the plane of the surface. The isotherm plotted in Figure 8 is well described by the linear form of the Langmuir equation:[19]

$$C_e/q_e = (1/q_{\max}.K_L) + (C_e/q_{\max}) \quad (2)$$

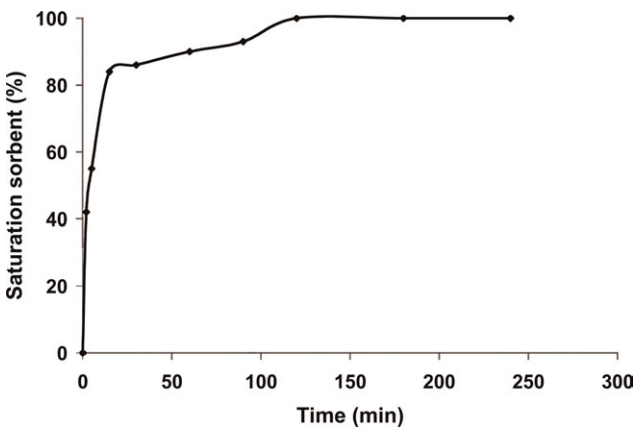

Figure 6. Kinetics of Nd(III) adsorptions on PAN-IDA fibers within 2–120 min time range at pH 6.

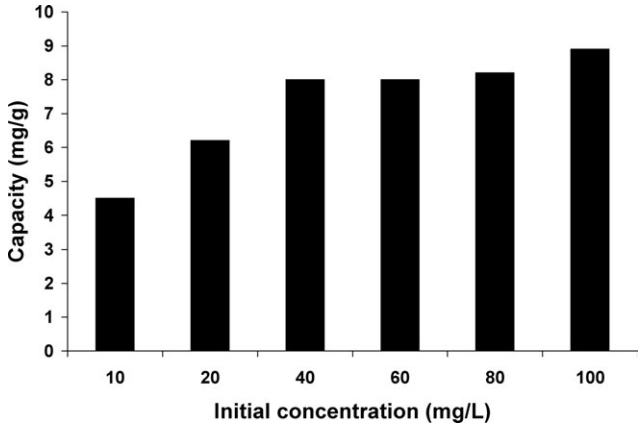

Figure 7. Effect of initial concentration of the Nd(III) in the solution on sorption capacity.

where C_e (mg L^{-1}) is equilibrium concentrations of Nd(III), q_e (mg g^{-1}) is amount of Nd(III) at equilibrium on PAN-IDA fiber, q_{max} is the maximum adsorption capacity corresponding to complete monolayer coverage on the surface (mg g^{-1}) and K_L is the Langmuir constant (L mg^{-1}) related to adsorption capacity and energy of adsorption, respectively. The constants can be evaluated from the intercepts and the slopes of the linear plots of C_e/q_e versus C_e (Figure 8). The data fitted well in the Langmuir equation as shown by the regression coefficient values ($R^2 = 0.9626$). The K_L and q_{max} values determined from the slopes ($1/q_{max}$) and intercepts ($1/q_{max}.K_L$) of the straight-line plot are 0.465 L mg^{-1} and 9.22 mg g^{-1}, respectively. Conformation of the experimental data in to Langmuir isotherm model indicates the homogeneous nature of PAN-IDA surface. The essential characteristics of a Langmuir isotherm can also be expressed in terms of a dimensionless constant separation factor R_L, given by the following equation: [20]

$$R_L = 1/(1 + K_L.C_0) \quad (3)$$

where C_0 is the initial metal concentration (mg/L) and K_L is the energy of interaction at the surface. For a favorable adsorption, the separation factor R_L lies between 0 and 1.

The calculated R_L value at optimum pH from above formula is 0.021 which confirms the favorable uptake of the Nd(III) from the solution.

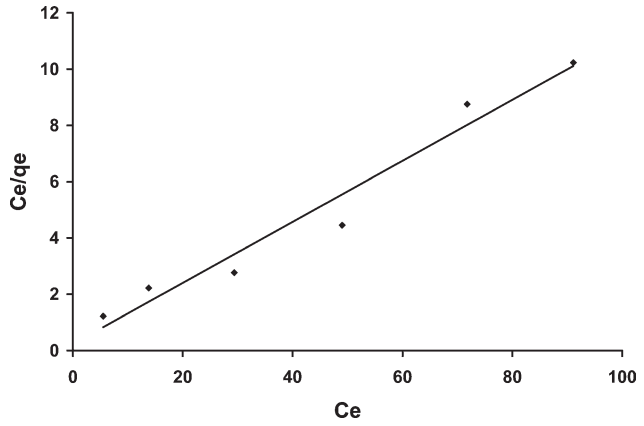

Figure 8. Langmuir isotherm for Nd(III) adsorption onto PAN- IDA at 20°C.

Table II. Effect of Other Ions on Sorption

Interfering ion	adsorbed Nd(III) (mg L^{-1})	Loss of adsorption (%)	Extraction percentage (%)	Distribution ratio
-	4.90	-	49.0	0.96
Sm(III)	4.88	0.4	48.8	0.95
Hg(II)	4.89	0.2	48.9	0.96
Cu(II)	3.65	25.5	36.5	0.57
Co(II)	4.86	0.8	48.6	0.95
Mn(II)	4.14	15.5	41.4	0.71
Mg(II)	3.90	20.4	39	0.64
Pb(II)	3.80	22.4	38	0.61
Zn(II)	4.9	-	49	0.96
Sn(II)	4.7	4.1	47	0.89
Na(I)	4.90	-	49.0	0.96
K(I)	4.90	-	49.0	0.96

Effect of Foreign Ions

To evaluate the selectivity of the preconcentration system, the effect of some metal ions (10 mg L^{-1}) on the sorption behavior of Nd(III) ion (10 mg L^{-1}) was investigated. The extraction percentage (E%) and the distribution ratio (D) were calculated from the following equations

$$Q = (C_0 - C_e)V/W \quad (4)$$

$$E = (C_0 - C_e)/C0 \quad (5)$$

$$D = Q/C_e \quad (6)$$

where Q represents the adsorption capacity (mg g^{-1}), C_0 and C_e represent the initial and equilibrium concentration of Nd(III) (μg mL^{-1}), W is the mass of sorbent (g), V is the volume of metal ion solution (L), E% is the extraction percentage, and D is the distribution ratio (mL g^{-1}). The result was shown in Table II. This Table indicates that the most effective ions on adsorption of Nd(III) PAN-IDA are Cu(II), Mg(II) and Pb(II). The effects of other mentioned foreign ions at given concentrations are negligible. The adsorption of Nd(III) on the modified PAN in presence of all mentioned ions (with each ion having the concentration of 10 mg L^{-1}) shows that the Nd(III) can be determined quantitatively in the environmental samples.

Application of Method

Modified PAN was used to preconcentrate and determine Nd(III) in water from The Zayandehroud river (Isfahan, Iran). The pH of water sample was adjusted to the optimum pH. ICP-AES was applied to determine the Nd(III) in water sample. As no Nd(III) was detected in the water sample, 100 mL water sample was spiked with Nd(III) before subjecting it to the recommended procedure. The results are shown in Table III. These results demonstrate the applicability of the procedure for neodymium determination in environmental samples with high recovery (>90%).

Adsorption of Nd(III) ions on the modified PAN fiber from human plasma was also studied batch wise. Human blood was

Table III. Results Obtained from Nd(III) Determination in Different Sample

	Human plasma	Zayandehroud river
Detected (μg mL^{-1})	N.D.	N.D.
Added (μg mL^{-1})	0.20	0.10
Found after preconcentration (μg mL^{-1})	0.74	0.93
Preconcentration factor	5	10
Recovery (%)	74	93
Standard deviation	0.033	0.012
RSD (%)[a]	4.5	1.3

[a]For three determinations.

collected from thoroughly controlled voluntary blood donors. Each unit separately controlled and found negative for hepatitis B surface antigen (HBsAg) and human immunodeficiency virus (HIV) I, II, and hepatitis C antibodies. Human blood was collected into test tube containing ethylenediaminetetraacetic acid and red blood cells were separated from plasma by centrifugation at 3500 × g for 30 min at room temperature, and then filtered frozen at −20°C. Before use, the plasma was thawed for 1 h at 37°C. After no detection of Nd(III) in the plasma, 25 mL plasma was spiked with Nd(III) before subjecting it to the recommended procedure. The experiments were performed in replicates of three. The results are shown in Table III and indicate the suitability of the present sorbent for the preconcentration of neodymium from plasma samples. The moderate recovery indicates a rather strong competition of plasma components for Nd(III) binding or blockage of binding sites on the resin by plasma components.

Comparison with Other Method

According to literature survey there is a few report about Nd(III) extraction or preconcentration. Kevin et al.[21] tried to analysis Nd(III) in groundwater samples by inductively coupled plasma mass spectrometry without any preconcentration. The precision of the method was 7% (R.S.D), so the method is not so precise rather than our method. In other experience, Persson et al.[22] reported a method for preconcentration and determination of isotopic composition of neodymium in aqueous samples. The method uses a resin, Nobias PA1 from Hitachi High-Technologies, which has a hydrophilic methacrylate polymer backbone where the functional groups ethylenediaminetriacetic and iminodiacetic acids are immobilized. A recovery of 90% was obtained with 0.5 M nitric acid as eluting agent. It is interesting that the immobilized ligand and eluting agent of both methods are the same. Although the method was so good, the recovery is lower than of our work.

CONCLUSION

A new chelating resin is prepared by grafting polyacrylonitrile fiber with iminodiacetic acid. The synthesis of the resin is simple and economical. The resin has a good potential for enrichment of trace amount of Nd(III) from large sample volumes. The sorption rate of the investigated metal ions on the sorbent was excellent. The sorption of the investigated metal ions increases by increasing the contact time. Based on the Langmuir isotherm analysis, the monolayer adsorption capacity was determined to be 9.22 (mg g^{-1}) at 20°C. The R_L values showed that the PAN-IDA fiber was favorable for the adsorption of Nd(III). Preconcentration by this modified fiber combined with ICP- AES can be applied to determination of trace neodymium ions in environmental sample with satisfactory results.

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