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Functionalization of polyacrylonitrile fiber by iminodiaceticacid for adsorption and removal of samarium ion from environmental samples

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Abstract: This paper reports resulting adsorption and removal of heavy metal via modification of polyacrylonitrile (PAN) with iminodiaceticacid (IDA). Scanning electron microscope (SEM), fourier transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA), were applied to characterize the polyacrylonitrile- iminodiaceticacid (PAN-IDA). Inaddition, PAN-IDA was employed for preconcentration and determination of trace Sm(III) ion from environmental water samples with inductively coupled plasma–atomic emission spectroscopy. The optimum pH value for sorption of the metal ion was 5.7 with 100% recovery. The sorption capacity of functionalized modified fiber was found 0.256 mg.g^{-1} for Sm(III). The functionalized fiber can be reused for 10 cycles of sorption–desorption without any significant change in sorption capacity. The equilibrium adsorption data of Sm(III) on modified fiber were analyzed by Freundlich, Temkin, and Redlich–Peterson models. The method was applied for samarium ions determination from real sample. The saturation adsorption capacity for samarium metal was measured 37.5 mg.g^{-1}. In addition, over 90% of metal ion was recovered from the metal-loaded PAN-IDA in 0.5 mol L^{-1} HNO$_3$ solution after one hour.

Introduction

Modification of acrylonitrile polymers based precursors, which have large specific surface areas and high adsorption rates and with the purpose of creating functional groups to establish steady coordination with heavy metals have been carried out by many researchers [1]. The variety of production processes including metal finishing, storage batteries, mining, galvanizing, the ceramic and glass industrial lead to formation of great quantities of wastewaters containing heavy metal ions [2-5].

These metals cause various ailments such as destroying the nervous systems of young children; lung irritation, eye irritation, skin rashes, and liver damage [6]. There are many methods to reduce the heavy metal content of effluence by chemical precipitation [7], ion exchange [8, 9], chelating fiber [10], and common adsorption [11, 12]. The separation or adsorption of trace metal ions from an aqueous solution has been considerable importance in different fields for solving wastewater problems, removing toxic metals from sea water and etc [13, 14]. Ion adsorption onto solid chelating polymer materials is one of the most techniques for separation and removal of metal ions from a wide variety of sources [15]. At present, commercial polyacrylonitrile (PAN), which are

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composed of at least 85% by weight of acrylonitrile (AN) units, are mainly used as a separation processes due to functionalizing groups. Polyacrylonitrile fiber (PANF) with an abundance of cyano groups can be easily transformed in to various functional groups (carboxyl, amide, amidoxime ,etc) [16-18]. Among them amide groups have high tendency to form strong complexes with a wide range of heavy metal ions such as lanthanides (La(III), Nd(III), and Sm(III)) [19]. As a As a result, a variety of chelating fibers based on (PANF) have been synthesized. In the present study, PAN fiber was modified by iminodiaceticacid to provide chelating fibers and prepared modified polyacrylonitrile (PAN-IDA) [20]. These chelating fibers were used for the adsorption of samarium metal ions. Prepared a polyacrylonitrile–iminodiaceticacid chelating fiber and used it for the preconcentration and separation of trace Samarium.

Result and discussion

Characterization of modified fiber:

FT-IR Measurements:

The infrared absorption of raw acrylic fibers (RAF), indicate absorptions at 2245 Cm^{-1} (CN), 2936 Cm^{-1} (CH stretching in CH, CH_2 , CH_3 groups), 1732 Cm^{-1} (C=O stretching),1449 Cm^{-1} (CH_2 blending),1000-1300 Cm^{-1} (C-O stretching in ester) (Figure **1a**). The IR spectrum of iminodiaceticacid loaded polyacrylonitrile is compared with that of free polyacrylonitrile (Figure **1b**). New peak at 1657 Cm^{-1} that is corresponding to C=O in amide group (-CO-NR_2) as well as additional bands at 1300, 1710, 3300 and 1465 cm^{-1} which appear due to placement of C-N, -CO-OH, OH, and CH_2 stretching vibration, respectively. Comparison between the IR spectrums of modified PAN with raw PAN is shown in Table **1**.

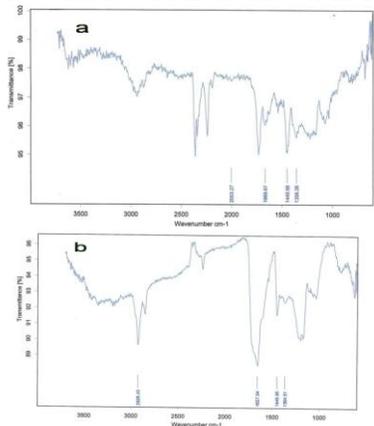**Figure 1:** FT-IR spectra of (a) raw acrylic fiber and (b) modified polyacrylonitrile fiber.

Table 1: The infrared frequency bands.

FT-IR (KBr, υ/cm^{-1})		
Characteristic group	Raw PAN	Modified PAN
υ (NH)		3300
υ (OH)	3500-3600	3300
υ (CH-CH_2-CH_3)	2850-3000	2850-3000
υ (CN)	2244	
υ (C=O)	1735	
υ (HNC=O)		1660
υ (HOC=O)		1730
υ (-CO-NHR)		1500
υ (C-O)	1000-1200	1100
υ (C-N)		1300
υ (C=C)		1650
υ (C=N)		1560-1640
υ (NH)		1500
υ (CH_2)	1465	1465
υ (CH)	1400	

Elemental analysis:

The procedures used in this study are reported in the thermogravimetric elemental-analyzer manual. The percentages of C, H, and N in the sample were determined after drawing the calibration curves for standards and processing data for the sample. The data of elemental analysis of raw PAN and modified PAN, are listed in Table **2**. This Table demonstrated that the percentage of nitrogen in modified PAN was lower than the raw PAN. This is due to conversion of C≡N groups to C-N(CH_2COOH)$_2$.

Table 2: Elemental analysis for Raw PAN and modified PAN (PAN-IDA).

CHN analysis	%C	%H	%N
Raw PAN	65.56	5.72	23.55

| Modified PAN | 55.70 | 5.76 | 15.28 |

Thermal Measurements:

The thermal behavior of the PAN-IDA in comparison with PAN was studied thermo gravimetric (Figure **2**). Raw acrylic fiber is decomposed in the temperature range of 300 to 500 °C and decomposition temperature range of PAN-IDA was 400°C. The thermo gravimetric data indicates that the initial thermal stability of PAN-IDA is a bit lower than that of raw acrylic fiber [4].
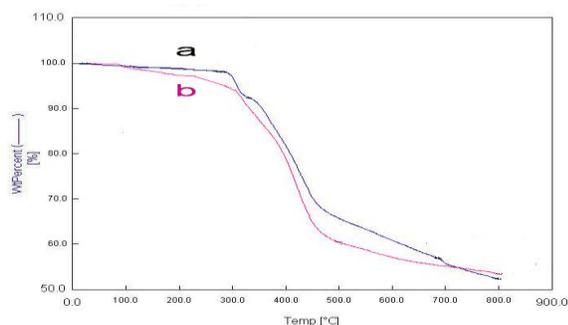

Figure 2: TGA of (a) raw PAN (b) modified PAN.

Morphologies of the RAF and PAN-IDA:

Scanning electron microscopy (SEM) images of the PAN before and after modification of fiber were shown in Fig.3. It is clear that changes have been occurred in the morphology of the fibers. Also, photographs demonstrated that the surface of PAN was approximately smooth and highly homogeneous as that of modified fiber because of grafting chelating ligand.
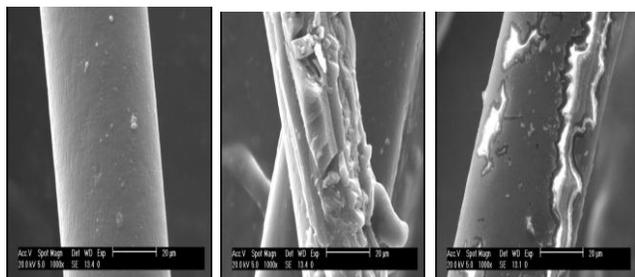

Figure 3: SEM images of (a) raw PAN (b and c) modified PAN.

Metal sorption as a function of pH:

The degree of metal sorption at different pH values was determined by batch equilibration technique. A set of solutions (volume of each 100 mL) containing 0.5 μg mL^{-1} of Sm (III) was taken. Their pH values were adjusted in the range of 4.5–9 with 0.01 M acetate and/or phosphate buffer solutions. The 0.1 g of polyacrilonitrile iminidiaceticacid (PAN-IDA) was

added to each solution and the mixture was shaken for 7 hour. The optimum pH values for quantitative uptake of metal ions were ascertained by measuring the Sm(III) content (by ICP-AES) in supernatant liquid and in the elute obtained by desorbing the metal ion from fiber with 0.5 M nitric acid (10 mL). The optimum pH range for the sorption of Sm(III) is shown in Figure **4**. The maximum recovery was 100% at pH 5.7.
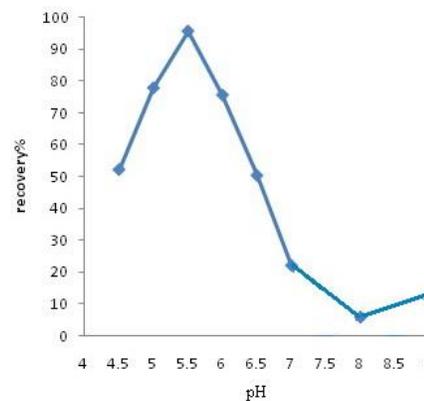

Figure 4: Effect of pH sorption of Sm (III) onto modified polyacrilonitrile.

Total sorption capacity:

The 0.05 g of fiber beads were stirred for 5 h with 50 mL solution containing 100 μg mL^{-1} of Sm (III), at optimum pH. The metal ion concentration in the supernatant liquid was estimated by ICP-AES. The sorption capacity of the fiber for the metal ion was ascertained from the difference between the metal ion concentrations in solution before and after the sorption. The saturated adsorption capacity of the modified fiber was found to be 0.256 mmol g^{-1} of fiber for Sm(III).

Desorption of metal ions from the metal loaded PAN-IDA:

The Sm(III) was sorbed and desorbed on 1 g of the fiber several times. An optimum concentration (0.5 mol/L) was selected for maximum desorption of the loaded metal. The sample solution was collected after stirring for 5, 15, 30, 60, 90, and 120 min, and then concentration of metal ions was determined. The resultant values indicated that the time of samarium adsorption equilibrium on PAN-IDA fibers was very fast and completed only about 50 min (Figure **5**). Also, the fiber cartridge after loading it with samples can be readily regenerated with 0.5 M HNO3.
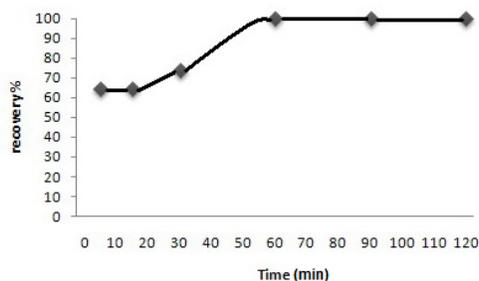
Figure 5: Optimum adsorbent time for modified polyacrilonitrile.

Adsorption isotherm:

The Freundlich equation is an empirical equation employed to the described heterogeneous systems, in which it is characterized by the heterogeneity factor $1/n$. Hence, the empirical equation can be written [21]:

$$q_e = K_F \cdot C_e^{1/n} \qquad (3)$$

where K_F is the Freundlich constant (mg/g) $(L/mg)^{1/n}$ and $1/n$ is the heterogeneity factor. *A* linear form of the Freundlich expression can be obtained by taking logarithms of Eq. (3):

$$Ln\ q_e = Ln\ K_F + 1/n\ Ln\ C_e \qquad (4)$$

Therefore, a plot of Ln q_e versus Ln C_e (Figure **6**) enables the constant K_F and exponent $1/n$ to be determined (Table **3**). The Freundlich equation predicts that the Sm (III) concentration on the adsorbent will increase so long as there is an increase in the Sm (III) concentration in the liquid.
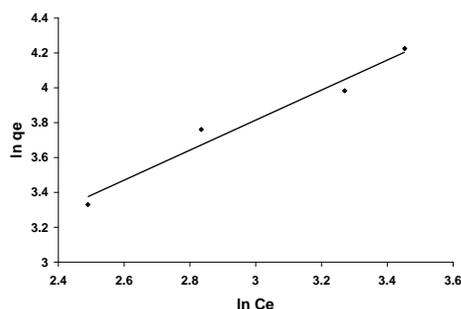

Figure 6: Freundlich isotherm for Sm (III) adsorption onto polyacrilonitrile iminodiaceticacid at 25°C.

The Temkin equation suggests a linear decrease of sorption energy as the degree of completion of the sorptional centers of an adsorbent is increased.

$$q_e = (RT/b)\ ln(AC_e) \qquad (5)$$

and can be linearized:

$$q_e = B\ lnA + B\ lnC_e \qquad (6)$$

where B=(RT)/b and b is the Temkin constant related to heat of sorption (J mol^{-1}). A is the Temkin isotherm constant (L g^{-1}), R the gas constant (8.314 Jmol^{-1} K^{-1}) and T is the absolute temperature (K). Therefore plotting q_e versus ln C_e (Figure **7**) enables the constants A and B. Temkin parameters calculated from Eqs. (5) and (6) are listed in Table **3**.
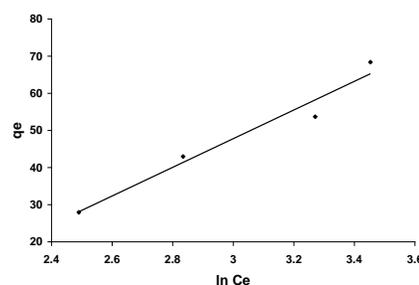

Figure 7: Temkin isotherm for Sm (III) adsorption onto polyacrilonitrile iminodiaceticacid at 25°C.

The Redlich–Peterson isotherm contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms. The Redlich–Peterson isotherm has a linear dependence on concentration in the numerator and an exponential function in the denominator.[22] It can be described as follows:

$$q_e = \frac{AC_e}{1 + BC_e^g}$$

It has three isotherm constants, namely, A, B, and g $(0 < g < 1)$, which characterize the isotherm. Its limiting behavior is summarized. Where $g = 1$, the Langmuir form results. Where, constants A and B are much greater than unity, the Freundlich form results. Three isotherm constants, A, B, and *g* can be evaluated using a trial and error procedure, which is applicable to computer operation was developed to determine the isotherm parameters by optimization routine to maximize the coefficient of determination. The Redlich–Peterson isotherm constants, A, B, and g for the sorption of Sm(III) on to modified fiber using the linear regression is shown in Table **3**.

Conclusion

A fiber was synthesized by coupling of polyacrylonitrile (PAN) with iminodiaceticacid (IDA). The synthesis of the fiber is simple and economical.

The fiber has a good potential for enrichment of trace amount of Sm(III) from large sample volumes. The Sm(III) adsorption was due to immobilized ligand–metal ion interactions. The fibers also present the advantage of high adsorption capacity, good reusability and high chemical stability. Based on the isotherm analysis, the adsorption capacity was determined to be 37.6 (mg.g^{-1}) at 25°C. The R_L values showed that the modified polyacrylonitrile was favorable for the adsorption of Sm (III). Preconcentration by this fiber combined with ICP-AES can be applied to the determination of trace Sm(III) ions in water and the mineral reference sample with satisfactory results. The sorption of metal ion takes place in moderate time, making the analytical procedure reasonably fast.

Table 3: Isotherm parameters obtained by using linear method for adsorption of Sm (III) at 25°C.

Frendlich isotherm model		
K_F (mg g^{-1}) (L mg^{-1})$^{1/n}$	n	R^2
3.4219	1.16	0.9665
Temkin isotherm model		
A (L g^{-1})	B	b (J mol^{-1})	R^2
67.995	38.593	64.197	0.9622
Redlich–Peterson isotherm model		
g	B(dm^3 mg^{-1})^g	A(dm^3 g^{-1})	R^2
0.15	10.7	40.0	0.9992

Experimental

FT-IR spectrums of the samples were recorded by Bruker spectrophotometer (VERTEX 70) model equipped with ATR cell. The pH measurements were made with Metrohm model 744 (Switzerland) pH meter. TAQ 50 derivatograph (Shimadzu, Japan) was used for thermogravimetric analysis (TGA). The concentration of samarium ion (Sm(III)) was determined using inductively coupled plasma-atomic emission spectrometer (ICP-AES), Varian Australia, Vista pro. Elemental analysis was carried out on an elemental analyzer from PerkinElmer model 2400 series II. Micrograph of the fibers before and after modification was taken using SEM (PHILIPS XL30).

Reagents and solutions:

Acetic acid, sodium acetate, sodium hydrogen phosphate, sodium dihydrogen phosphate, samarium nitrate (Sm(NO$_3$)$_3$.6H$_2$O), hydrochloric acid, sulfuric acid, nitric acid, sodium nitrite, sodium hydroxide, and iminodiaceticacid, were products of Merck (Darmstadt, Germany). All the solutions were prepared in deionized water using analytical grade reagents. The stock solution (500 mg L^{-1}) of Sm(III) was prepared by dissolving appropriate amounts of samarium nitrate in deionized water. Ten milliliters of 0.01 M acetic acid acetate buffer (pH 3–5) and 0.01 M phosphate buffer (pH 6–9) were used to adjust the pH of the solutions, wherever suitable. Polyacrylonitrile fiber, contains 93.5 % wt acrylonitrile and 6.5% wt of methyl methacrylate, was obtained from polyacryl company, Esfahan, Iran.

Method:

Synthesis of chelating fiber:

Functionalization of chelating fiber containing monoamide ligands was prepared via the stepwise modification of polyacrylonitrile (PAN), with iminodiaceticacid (IDA), which can be divided into three main stages of processing. The first stage of modification was performed to remove residual from the PAN. Hence, to gain a pure clean sample of fibers, polyacrylonitrile fibers (0.1 g) were treated with 10 mL dichloromethane and the mixture was stirred and refluxed at 48°C for 15 hour. Then the mixture was directly filtered and dried at room temperature. In the second stage, lipid free PAN fibers (0.1 g) were added to a solution of H$_2$SO$_4$ (0.5 mL) in ethanol (1.5 mL) and the mixture was cooled in an ice bath. It was stirred under reflux for 15 hour then quenched with cold water. After removal of the solvent, fibers were dried at room temperature. A solution of NaOH (0.1 g) in H$_2$O (1.5 mL) was added to dried fibers and the mixture was refluxed for additional 15 h. Then, H$_2$O (0.5 mL) was added. Under cooling condition the resulted mixture was acidified by H$_2$SO$_4$ (0.1 mL, 50% w/w). Then, it was filtered, washed with water and dried at room temperature. In final stage of modification, into a two necked flask equipped with condenser and separator funnel, thionyl chloride (5 mL) was added dropwise to PAN fibers (0.1 g) within 30 minutes. The resulted mixture was stirred under reflux for 5 hour. After that, it was filtered, washed with water and dried at room temperature. Then, a solution of 0.3 g. IDA in 10 ml. H$_2$O was added drop wise to the dried fibers and the resulted mixture was

stirred in an ice bath for 2 hr. Finally it was filtered and dried at room temperature. A schematic illustration of the procedure used to synthesize the modified polyacrilonitrile (PAN-IDA) is presented in Figure **8**.
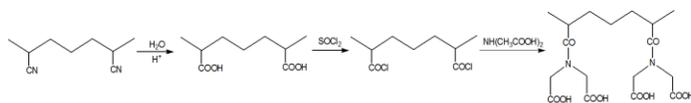

Figure 8: The synthesize of modified polyacrilonitrile (PAN-IDA).

Batch method:

A sample solution (100 mL) containing (0.5 μg mL^{-1}) of Sm (III) was taken in a glass stoppered bottle, after adjusting its pH to the optimum value. The 0.05 g of PAN-IDA was added to the bottle and the mixture was shaken for optimum time. The modified fiber was filtered and sorbed the metal ion was eluted with 0.5 M HNO$_3$ (10 mL). The concentration of the metal ion in elute was determined by ICP-AES. The wavelength of 359.259 nm was used for Sm(III) determination.

Isotherm studies:

Isotherm studies were carried out by adding a fixed amount of adsorbent (0.05 g) to a beaker filled with 25 mL diluted solution of Sm (III) (10-100 μg mL^{-1}). The beaker was then sealed and placed in a water bath shaker and shaken at 200 rpm with a required adsorbent time (4h) at 25°C and an optimum pH of 5.7. Adjustments of pH have been done using 0.01M acetate buffer. The beaker was then removed from the shaker, and the final concentration of Sm (III) in the solution was measured by ICP-AES. The amount of Sm (III) at equilibrium q_e (mg.g^{-1}) on modified polyacrylonitrile fiber was calculated from the following equation:

$$q_e = (C_0 - C_e) \, V / W \qquad (1)$$

where C_0 and C_e (mg/L) are the liquid phase concentrations of Sm (III) at initial and equilibrium, respectively, V *(L)* the volume of the solution and W *(g)* is the mass of adsorbent used.

Acknowledgements

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