

Modification and Characterization of Poly (ethylene terephthalate)-Grafted-Acrylic Acid/Acryl Amide Fiber for Removal of Lead from Human Plasma and Environmental Samples

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ABSTRACT: A new fibrous adsorbent was prepared by grafting acrylic acid/acryl amide (AA/AAm) comonomers onto poly (ethylene terephthalate) (PET) fibers. The resulting sorbent has been characterized by Fourier transform infrared (FT-IR), elemental analysis, thermogravimetric analysis (TGA), FT-Raman, and scanning electron microscopy (SEM) and studied for the preconcentration and determination of trace Pb (II) ion from human biological fluid and environmental water samples. The optimum pH value for sorption of the metal ion was 8. The sorption capacity of functionalized resin is 44.1 mg g⁻¹. The chelating sorbent can be reused for 20 cycles of sorption-desorption without any significant change in sorption capacity. A recovery of 100.2% was obtained for the metal ion with 0.5M nitric acid as eluting agent. Effect of grafting yield, shaking time, shape of sorbent,

and pH of the medium on adsorption of the metal ion were investigated. Scatchard analysis revealed that the homogeneous binding sites were formed in the polymers. The equilibrium adsorption data of Pb (II) on modified fiber were analyzed by Langmuir, Freundlich, Temkin, and Redlich-Peterson models. Based on equilibrium adsorption data, the Langmuir, Freundlich, and Temkin constants were determined as 0.236, 10.544, and 9.497 at pH 8 and 20°C, respectively. The method was applied for lead ions determination from human plasma and sea water sample. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 5236–5246, 2012

Key words: solid-phase extraction; poly (ethylene terephthalate)-grafted-acrylic acid/acrylamide fiber; lead; polymer grafting; isotherm study; preconcentration

INTRODUCTION

Recently, heavy metals pollution in natural water has been receiving tremendous attention. The toxic heavy metals such as Pb, Cd, Hg are insignificant elements in human body and are capable of causing ecological risk to aquatic organisms. The toxic heavy metals could also gradually accumulate in human body through food chain and cause damage to human health.¹ Lead accumulates in the skeleton, especially in bone marrow. It is a neurotoxin and causes behavioral abnormalities, retarding intelligence, and mental development. It interferes in the metabolism of calcium and vitamin D and affects hemoglobin formation and causes anemia.² In view of the above facts, accurate determination of heavy metals has become increasingly necessary to solve the

problems connected with environmental water pollution.

However, the direct determination of these elements in real samples is a difficult task. The main restrictions come from the complexity of the matrix and the extremely low concentrations of analytes in those samples, which are often below the detection limits of available techniques. Thus, highly sensitive and selective techniques are required. Although the sensitive and accurate determination of trace elements by some instrumental techniques including inductively coupled plasma mass spectrometry, graphite furnace atomic absorption spectrometry is possible, flame atomic absorption spectrometry^{3,4} is preferred for trace element determination due to its cheap cost and simplicity. However, the determinations of elements at $\mu\text{g L}^{-1}$ concentration level by flame atomic absorption spectrometry are not possible. To solve this problem, preconcentration-separation procedures have been proposed. Preconcentration is a very important issue for achievement of low detection limits.^{5,6} There are many methods of preconcentration and separation such as liquid-liquid extraction,⁷

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ion exchange techniques,⁸ coprecipitation,⁹ membrane filter techniques,¹¹ cloud point extraction,^{12,13} and solid-phase extraction.^{14–16}

One trend in modern civilization is to effect gradual replacement of natural materials with either all synthetic materials or modified natural materials. In the polymeric age, it is essential to modify the properties of a polymer according to tailor-made specifications designed for target applications. There are several means to modify polymers properties, *via* blending, grafting, and curing. "Blending" is the physical mixture of two (or more) polymers to obtain the requisite properties.¹⁷ "Grafting" is a method wherein monomers are covalently bonded (modified) onto the polymer chain, whereas in curing, the polymerization of an oligomer mixture forms a coating which adheres to the substrate by physical forces.

Fibrous reactive materials have a very high adsorption capacity due to their very large surface area.¹⁸ There are mainly two ways to prepare reactive fibers, namely, the exchange of the existing groups on the fiber with other reactive groups having higher adsorption ability and grafting of various vinyl monomers on the fiber by graft copolymerization. Grafting improves the adsorption capacity and selectivity of fiber significantly by forming many reactive groups upon the polymer chains, so the grafting on fibers like poly (ethylene terephthalate) (PET) is still interested.^{19–22}

The purpose of this study is to indicate the feasibility of using PET-acrylic acid/acryl amide (AA/AAm) fiber as a solid-phase extractant for preconcentration of trace lead in biological fluid and environmental water samples. Trace lead can be retained on the surface of PET-AA/AAm fiber and then desorbed with 0.5M nitric acid before determination by FAAS. This proposed novel method has advantages of good accuracy and precision, high recovery, and preconcentration factor.

EXPERIMENTAL

Instruments

A flame atomic absorption spectrometer (Varian, AA240) equipped with air-acetylene flame (air and acetylene flow rate: 8 and 1.7 L min⁻¹, respectively) and inductive couple plasma-atomic emission spectroscopy (ICP-AES), Varian, model Vista were used for concentration measurement of metal ions. The pH measurements were made with a Metrohm model 744 pH meter (Zofingen, Switzerland). Infrared spectra were recorded on a Jasco Fourier transform infrared spectrometer (FT-IR-410, Jasco, Easton, Maryland). Elemental analysis was carried out on a Thermo-Finnigan (Milan, Italy) model Flash EA ele-

mental analyzer. Thermogravimetric analysis (TGA) was carried out by using a TGA-50H (Shimadzu Corp.). The SEM micrographs were obtained on a SEM-PHILIPS XL30 scanning electron microscopy (SEM).

Reagents and solutions

Fiber PET (filaments: 130 and dtex 170) made in Textile Engineering Department, Amir Kabir University of technology, Tehran, Iran.

Acrylic acid, acryl amid, benzoyl peroxide, acetone, Pb(NO₃)₂, NaH₂PO₄, Na₂HPO₄, CH₃COONa, HgCl₂, SnCl₂·2H₂O, FeSO₄·7H₂O, KCl, Co(N-O₃)₂·6H₂O, CaCl₂, AgNO₃, Mg(NO₃)₂·6H₂O, ZnSO₄, HNO₃, CH₃COOH, and CuSO₄·5H₂O were products of Merck (Darmstadt, Germany).

All the reagents were analytical grades and used without any further purification. The stock solution (1000 mg L⁻¹) of Pb (II) was prepared by dissolving appropriate amounts of Pb (NO₃)₂, in deionized water. The 0.01M acetic acid-acetate buffer (pH 3–6.5), 0.01M phosphate buffer (pH 6.5–9) were used to adjust the pH of the solutions, when needed.

Synthesis of PET-AA/AAm fiber

Fiber samples (0.100 ± 0.001 g) were placed in a 100 mL polymerization tube and calculated amount of AA and AAm were added to it. Then Bz₂O₂ dissolved in 3 mL acetone was added to tube. The mixture was made up to 50 mL with deionized water and placed into a water bath at the polymerization temperature 85 ± 1°C for 2 h. The fiber samples taken at the end of polymerization were freed from homopolymer or copolymers by washing with boiling water and acetone for 1 h (changing the washing water four times). The washed fiber was dried at 50°C under vacuum. The methodology used to synthesize modified PET is summarized in Figure 1.

Batch method

A sample solution (50 mL) containing (0.3 µg mL⁻¹) of Pb (II) was taken in a glass stoppered bottle, and the pH was adjusted to optimum value. The 0.1 g of PET-AA/AAm fiber was added to the bottle and the mixture was shaken for optimum time. The resin was taken out and sorbed metal ion was eluted with 0.5M nitric acid (10 mL). The concentration of the metal ion in the eluant was determined by FAAS.

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 Pb (II) (10–100

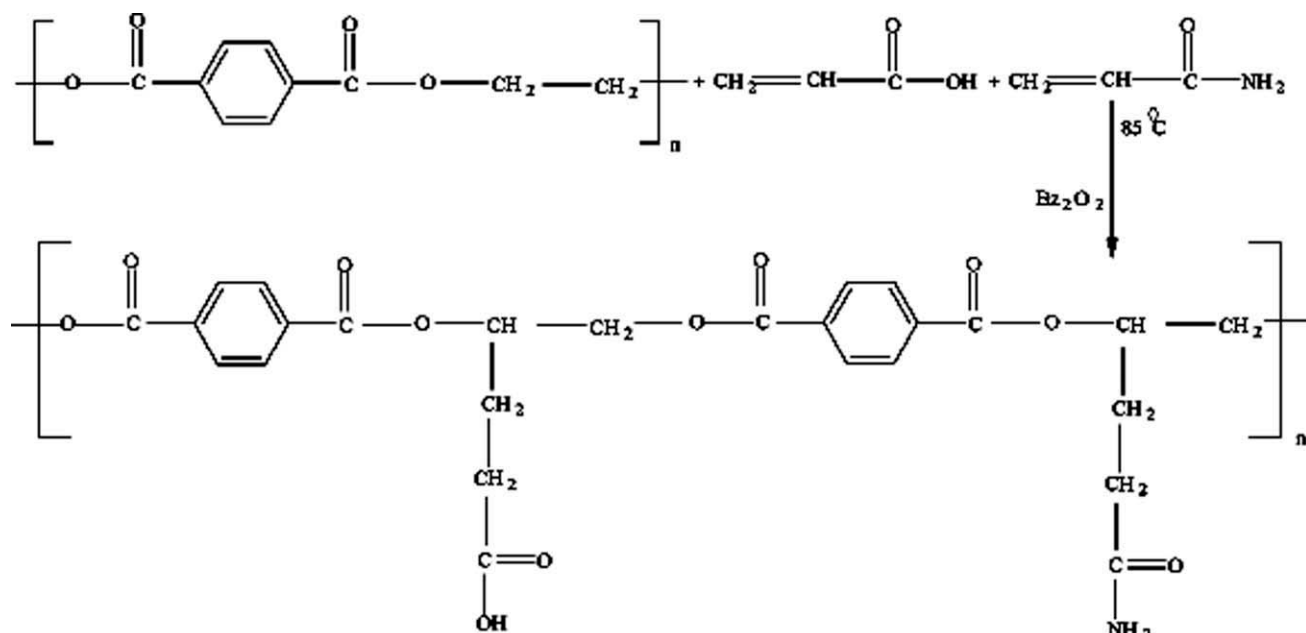


Figure 1 Schematic representation of the methods of polymer modification.

$\mu\text{g mL}^{-1}$). The beakers were then sealed and placed in a water bath shaker and shaken at 200 rpm with a required adsorbent time (4 h) at 20°C and optimum pH (8). pH adjustments have been done using 0.01M acetate buffer. The beakers were then removed from the shaker, and the final concentration of Pb (II) in the solution was measured by FAAS. The amount of Pb (II) at equilibrium q_e (mg/g) on PET-AA/AAM fiber was calculated from the following equation:

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

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

RESULTS AND DISCUSSION

Characterization of modified PET

IR Spectrum

The IR spectrum of PET-AA/AAM is compared with free PET (Fig. 2). There are two additional bands at $2096\text{--}3078$ and 1787 cm^{-1} which appear to originate due to NH_2 and amidic $\text{C}=\text{O}$.

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 con-

verted 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 (TCD). 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.

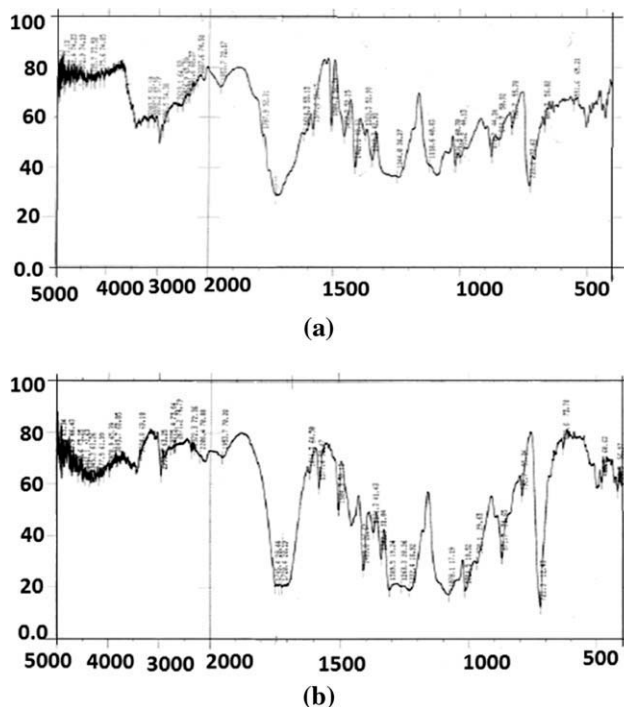


Figure 2 FT-IR spectrum of PET (a) and PET-AA/AAM (b).

The elemental analysis for PET (found: C, 62.08; H, 8.20; N, 0%, calculated for $(C_{10}H_8O_4)_n$: C, 62; H, 8.69; N, 0%) and PET-AA/AAM fiber (found: C, 61.37; H, 4.31; N, 1.16%, calculated for $(C_{10}H_8O_4)_5(C_3H_5O_2)_m(C_3H_6ON)_n$: on condition that $m = n = 1$: C, 61.36; H, 3.74; N, 1.27%) show that on an average one acrylic acid/acryl amide molecules are present in each five repeated unit of the polymer.

Thermal analysis

The thermal behavior of the PET-AA/AAM fiber in comparison with raw PET fibers was studied by thermogravimetry and differential thermogravimetry (TG-DTG) analysis (Fig. 3). The thermal decomposition of PET-AA/AAM fiber and raw PET proceed in three steps. For PET-AA/AAM decomposition, temperatures corresponding to the maximum rate of the mass loss are 408.8, 429.5, and 451.7°C and total mass loss is 89.7 wt %. The same values for the raw PET are 410.2, 432.7, 465.1°C, and 88.8 wt %. The beginning and end temperature in each decomposition steps of PET-AA/AAM are 350–425, 375–460, and 450–470°C. The values for three steps of raw PET are 355–436.1, 380–465, and 455–475°C. The overall mass loss in the PET-AA/AAM and raw PET samples were similar. The thermogravimetric data indicate that the initial thermal stability of PET-AA/AAM is lower than that of raw PET due to joining of the AA and AAM onto PET. In other words, the lower thermal stability PET-AA/AAM is due to the detachment of chemically immobilized moiety from the polymeric matrix.

Raman spectroscopy

Raman spectrum of PET-AA/AAM (cm^{-1}): 1612 aromatic (C=C), 1728 (amidic C=O), 1058 and 1117 (C–O), 3000 aromatic (C–H) and both 2996 and 3100 (NH_2).

Raman spectrum of PET-AA/AAM loaded Pb (II) (cm^{-1}): 1611 aromatic (C=C), 1732 (amidic C=O), 1085, 1125 (C–O), 3003 aromatic (C–H) and both 2965 and 3100 (NH_2).

The band observed in the PET-AA/AAM at 2996, 1728, 1117 cm^{-1} can be assigned to (NH_2) stretching vibration, (C=O) and (C–O) shift to 2965, 1732, and 1127 cm^{-1} in PET-AA/AAM– Pb^{+2} , respectively. These results demonstrate the amidic and acidic groups on the grafted polymer interact with Pb^{+2} and confirm the formation of PET-AA/AAM– Pb^{+2} complex.

Scanning electron microscopy

SEM was used to examine the external surface of the fiber after modification and metal ions adsorption.

The SEM images are presented in Figure 4. The surface of ungrafted PET has a smooth and highly homogeneous appearance. As shown in Figure 4(a,b), in comparison with the surface of the grafted PET, surface of raw PET were less coarse and groovy because PET-AA/AAM fiber have grafted chains containing AA and AAM. As seen in Figure 4(c), surface debris on the fibers after metal cation impregnation were observed. This image shows that ion adsorption increases the surface roughness. There is also an increase in diameter of the modified fibers. This can be related to the swelling phenomenon.

The effect of the monomer mixture ratios on grafting percentage

To investigate the effect of monomer mixture ratios on the grafting, the graft copolymerization was carried out at different W/V percentage ratios of AA/AAM co monomers by using Bz_2O_2 . The experimental results are shown in Figure 5. As seen from Figure 5, when AA was grafted alone on PET fibers the maximum grafting percentage was found to be as low as 6.94%. This suggests that AA is not sufficiently reactive toward PET macro radicals. Thus, the amount of AA in PET structure is lower. The use of AAM co monomer in grafting caused an increase in grafting percentage (9.98%). The grafting percentage was highly dependent on the monomer mixture ratio, and the maximum grafting percentage (16.34%) was reached at an AA/AAM ratio of 30:70. On the fibers grafted with the AA/AAM mixture, the side chains contained structural units coming from both AAM and AA.

Metal sorption as a function of pH

The grafted fiber SPE sorbents retains the analyte through a primary mechanism, such as electrostatic forces. However, backbone of sorbents often exhibit retention by a secondary mechanism as well, like van der Waals interactions, polar dipole–dipole forces or hydrogen bonding. PET-AA/AAM fibers primarily exhibit electrostatic interactions with metal ion, so the metal sorption can be affected by pH.

The degree metal sorption at different pH values was determined by batch equilibration technique. A set of solutions (the volume of each 100 mL) containing 0.5 $\mu g mL^{-1}$ of Pb (II) was taken. Their pH values were adjusted in range 3–9 with 0.01M acetate and/or phosphate buffer solutions. The 0.1 g of PET-AA/AAM fiber was added to each solution and the mixture was shaken for 6 h. The optimum pH values for quantitative uptake of metal ions were ascertained by measuring the Pb (II) content (by FAAS) in supernatant liquid and in the eluate

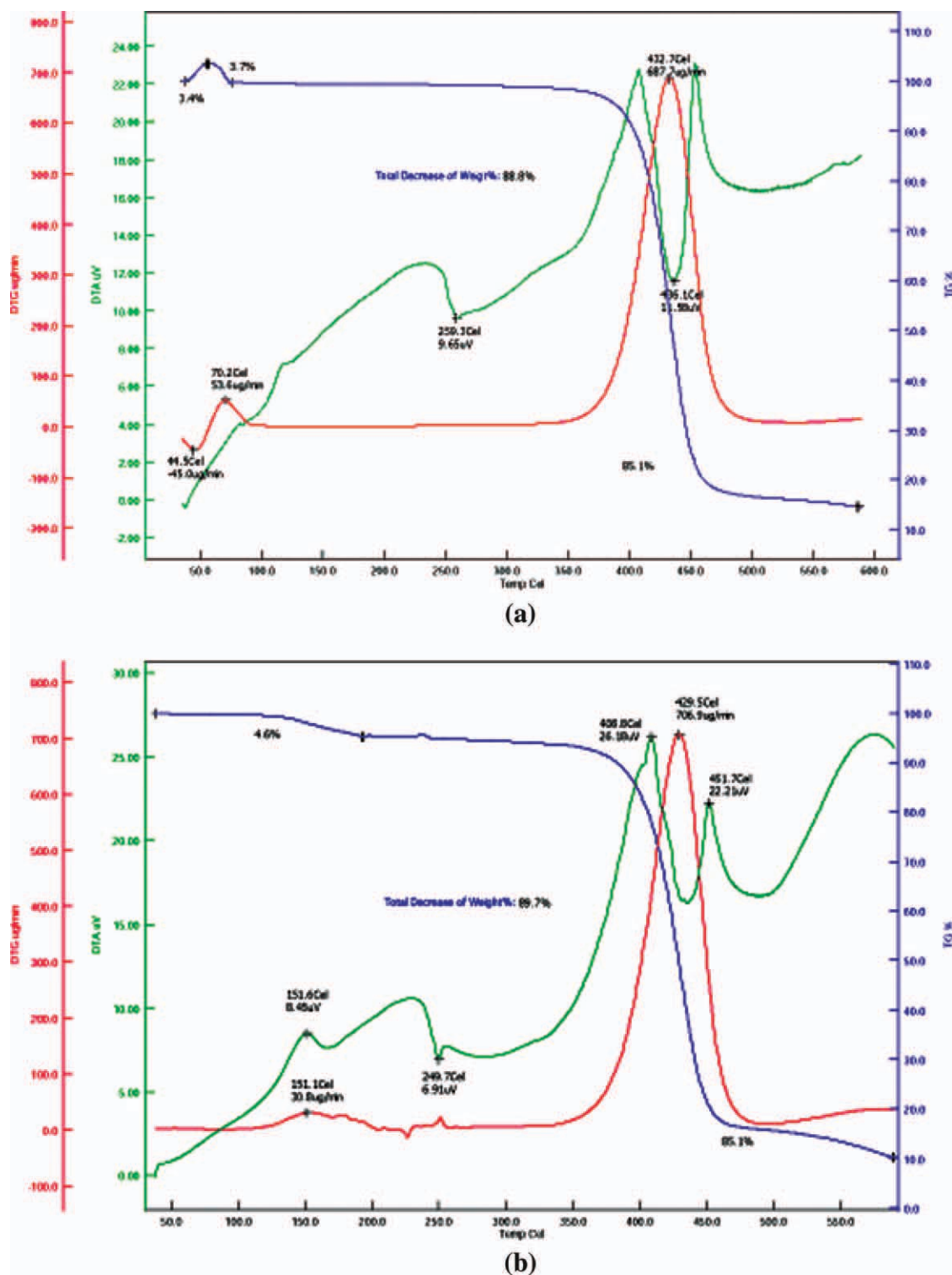
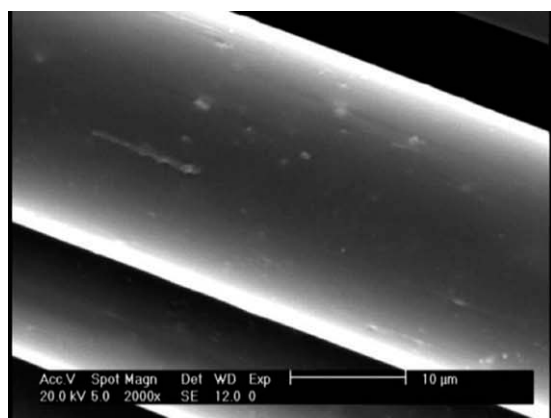


Figure 3 Thermogravimetry and differential thermogravimetry (TG-DTG) analysis of PET (a) and PET-AA/AAm (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

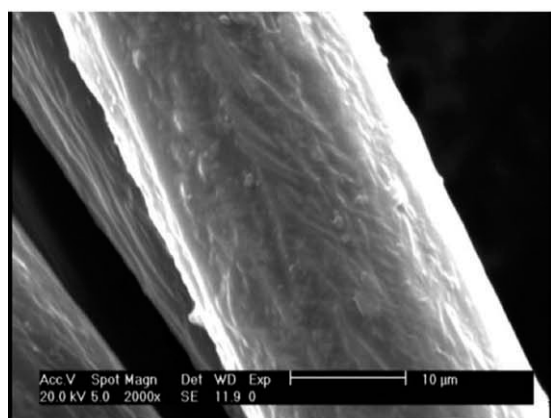
obtained by desorbing the metal ion from PET-AA/AAm fiber with 0.5M nitric acid (10 mL). The optimum pH range for the sorption of the metal ion is shown in Figure 6. The maximum recovery was 100.2% at pH 8.

Total sorption capacity

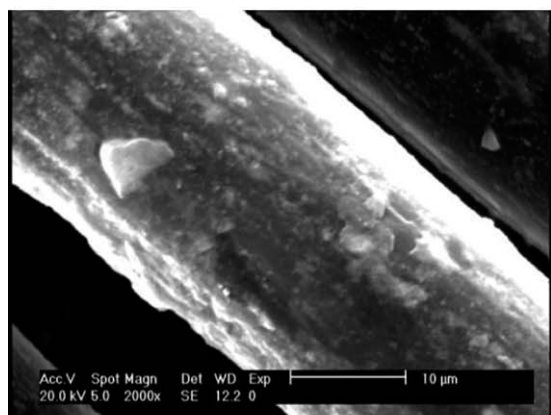
The 0.1 g of PET-AA/AAm fiber were stirred for 4 h with 50 mL solution containing 20–140 $\mu\text{g mL}^{-1}$ of Pb (II) at optimum pH and 20°C. The metal ion concentration in the supernatant liquid was estimated



(a)



(b)



(c)

Figure 4 SEM photograph of PET (a), PET-AA/AAm (B) and PET-AA/AAm loaded with metal ion.

by FAAS. The sorption capacity of the sorbent 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 resin was shown in Figure 7. This Figure indicates the effect of initial concentration of the Pb (II) in the solution on capacity sorption of Pb (II) by PET-AA/AAm fiber. The capacity

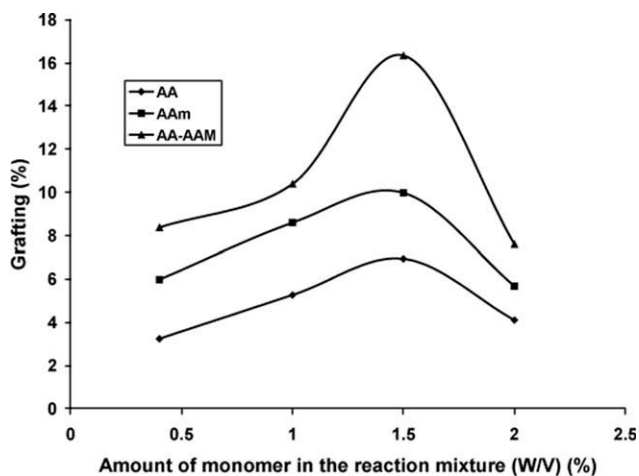


Figure 5 Effect monomer concentration on grafting percentage.

goes up with increasing initial concentration of the Pb (II) in the solution and gets constant after concentration of $100 \mu\text{g mL}^{-1}$ of Pb (II) (44.1 mg g^{-1}).

Stability and reusability of the sorbent

The Pb (II) was sorbed and desorbed on 1 g of the PET-AA/AAm fiber several times. It was found that sorption capacity of resin after 20 cycles of its equilibration with Pb (II), changes less than 10%. Therefore, repeated use of the resin is feasible. The resin after loaded with samples can be readily regenerated with 0.5M HNO₃. The sorption capacity of the resin stored for more than 6 months under ambient conditions has been found to be practically unchanged.

Optimization of sorption time of lead ions

PET-AA/AAm fiber (0.1 g) was shaken with 50 mL of solution containing $60 \mu\text{g mL}^{-1}$ of Pb (II) for different length of time (5, 15, 30, 45, 60, 90, and 120 min) under optimum pH. After taking out the

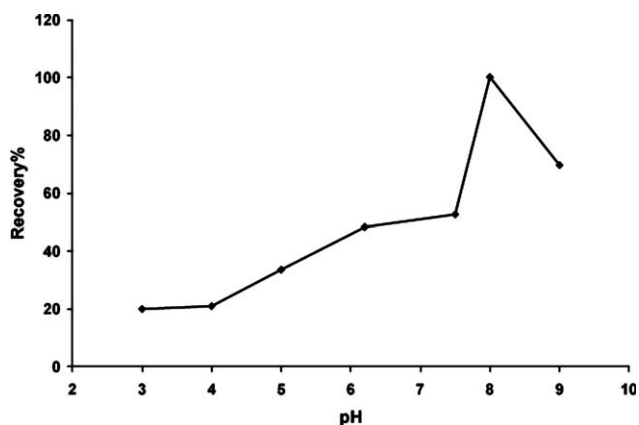


Figure 6 Effect of pH sorption of Pb (II) onto PET-AA/AAm.

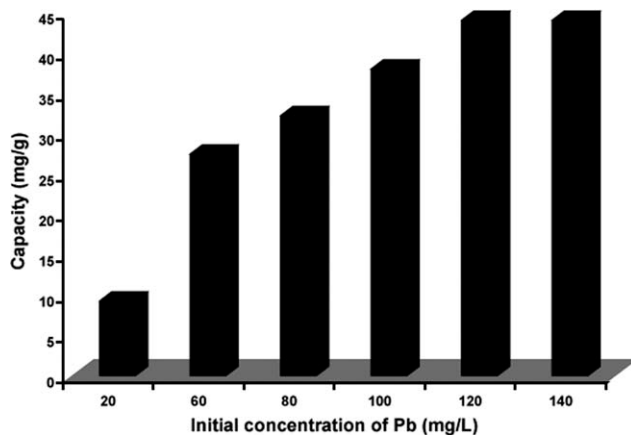


Figure 7 Effect of initial concentration of the Pb in the solution on capacity sorption of Pb (II) onto PET-AA/AAM.

sorbent, the concentration of lead ions in solution was determined with FAAS using the recommended batch method. The sorption as a function of contact time for all the metal ions is shown in Figure 8. Less than 5 min shaking was required for 90% sorption. The profile of lead uptake on this sorbent reflects good accessibility of the chelating sites in the PET-AA/AAM fiber.

Adsorption isotherms

The Langmuir equation is given in the following form²³:

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

where q_{\max} is the maximum adsorption capacity corresponding to complete monolayer coverage on the surface (mg/g) and K_L is the Langmuir constant (L/mg). The eq. (2) can be rearranged to a linear form:

$$C_e/q_e = (1/q_{\max} \cdot K_L) + (C_e/q_{\max}) \quad (3)$$

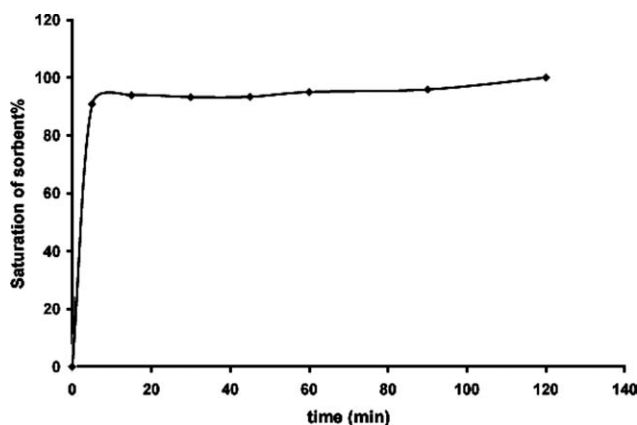


Figure 8 Kinetics of lead sorption on PET-AA/AAM.

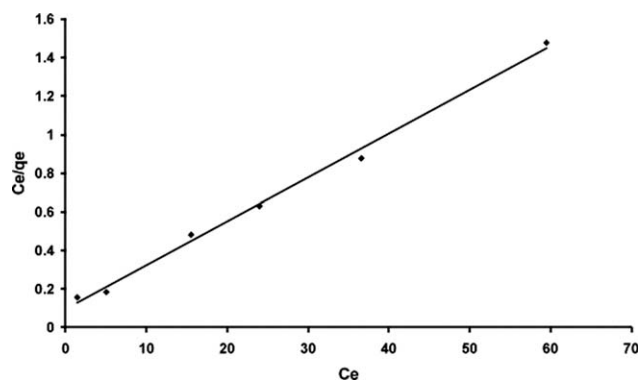


Figure 9 Langmuir isotherm for Pb (II) adsorption onto PET-AA/AAM at 20°C.

The constants can be evaluated from the intercepts and the slopes of the linear plots of C_e/q_e versus C_e (Fig. 9).

Conformation of the experimental data into Langmuir isotherm model indicates the homogeneous nature of PET-AA/AAM fiber surface. Langmuir parameters calculated from eq. (3) are listed in Table I.

The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless separation factor, R_L , defined as²⁴:

$$R_L = 1 / [(1 + K_L) \times C_0] \quad (4)$$

Table I shows that the value of R_L (0.041) is in the range of 0–1 at optimum pH which confirms the favorable uptake of the Pb (II).

The Freundlich equation is an empirical equation employed to describe heterogeneous systems, in which it is characterized by the heterogeneity factor $1/n$. Hence, the empirical equation can be written as:²⁵

$$q_e = K_F \times C_e^{1/n} \quad (5)$$

where K_F is the Freundlich constant (mg/g) (L/mg)^{1/n} and $1/n$ is the heterogeneity factor. A linear

Langmuir isotherm model			
q_{\max} (mg/g)	K_L (L/mg)	R_L	R^2
44.05	0.236	0.041	0.995
Freundlich isotherm model			
K_F (mg/g) (L/mg) ^{1/n}	n	R^2	
10.544	2.624	0.848	
Temkin isotherm model			
A (L/g)	B (J/mol)	b (J/mol)	R^2
2.29	9.497	256.49	0.961
Redlich–Peterson isotherm model			
g	B (dm ³ /mg) ^g	A (dm ³ /g)	R^2
1.06	0.132	8	0.987

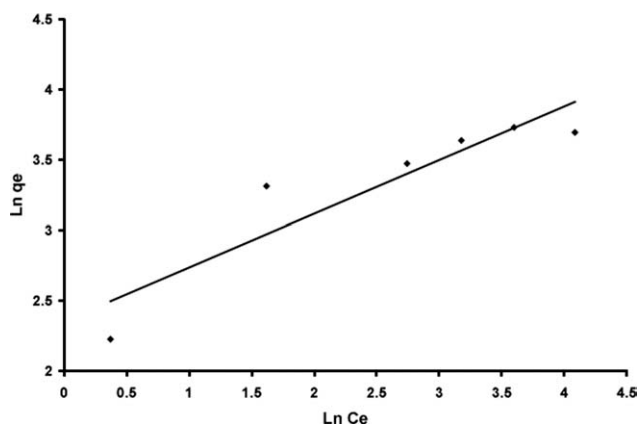


Figure 10 Freundlich isotherm for Pb (II) adsorption onto PET-AA/AAM at 20°C.

form of the Freundlich expression can be obtained by taking logarithms of the eq. (5):

$$\ln q_e = \ln K_F + (1/n) \ln C_e \quad (6)$$

Therefore, a plot of $\ln q_e$ versus $\ln C_e$ (Fig. 10) enables the constant K_F and exponent $1/n$ to be determined. The Freundlich equation predicts that the Pb (II) concentration on the adsorbent will increase so long as there is an increased in the Pb (II) concentration in the liquid.

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

The Temkin isotherm has been generally applied in the following form:

$$q_e = (RT/b) \ln (A \times C_e) \quad (7)$$

and can be linearized:

$$q_e = B \ln A + B \ln C_e \quad (8)$$

where $B = RT/b$ and b is the Temkin constant related to heat of sorption (J/mol). A is the Temkin isotherm constant (L/g), R the gas constant (8.314 J/mol K), and T is the absolute temperature (K). Therefore, plotting q_e versus $\ln C_e$ (Fig. 11) enables one to determine the constants A and B . Temkin parameters calculated from eqs. (7) and (8) are listed in Table I.

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. It can be described as follows:

$$q_e = \frac{AC_e}{1 + BC_e^g} \quad (9)$$

It has three isotherm constants, namely, A , B , and g ($0 < g < 1$), which characterize the isotherm. Its limiting behavior is summarized as follows:

where $g = 1$

$$q_e = \frac{AC_e}{1 + BC_e} \quad (10)$$

i.e., the Langmuir form results.

where constants A and B are much greater than unity²⁶

$$q_e = \frac{AC_e}{1 + BC_e^g} \quad (11)$$

i.e., the Freundlich form results.

where $g = 0$

$$q_e = \frac{AC_e}{1 + B} \quad (12)$$

i.e., the Henry's Law form results.

Equation (9) can be converted to a linear form by taking logarithms:

$$\ln \left(A \frac{C_e}{q_e} - 1 \right) = g \ln (C_e) + \ln(B) \quad (13)$$

Three isotherm constants, A , B , and g can be evaluated from the linear plot represented by eq. (13) using a trial and error procedure, which is applicable to computer operation. It was developed to determine the isotherm parameters by optimization routine to maximize the correlation coefficient, R^2 , for a series of values of A for the linear regression of $\ln (C_e)$ on $\ln[A(C_e/q_e) - 1]$ and to obtain the best value of A which yields a maximum "optimized" value of R^2 using the solver add-in with Microsoft's spreadsheet, Microsoft Excel.

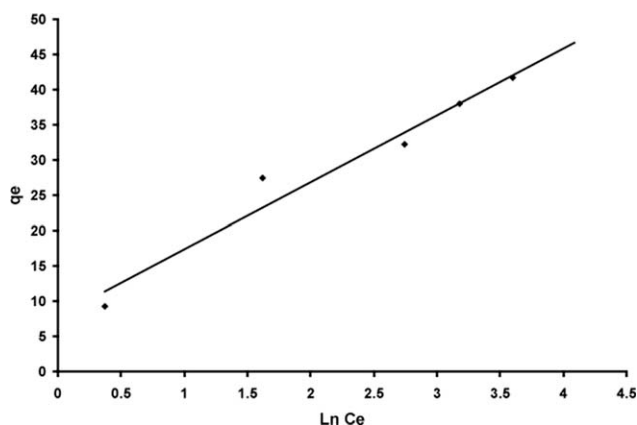


Figure 11 Temkin isotherm for Pb (II) adsorption onto PET-AA/AAM at 20°C.

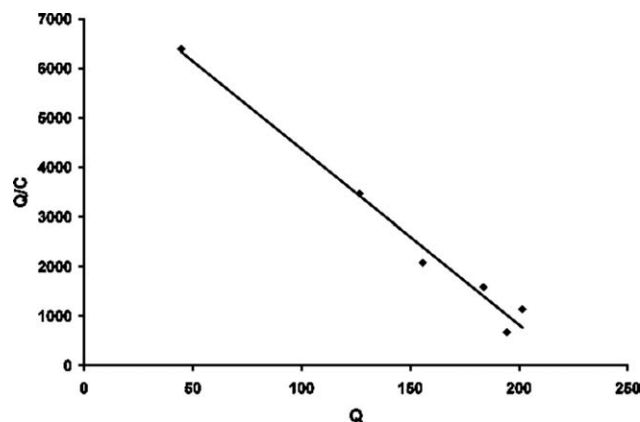


Figure 12 Scatchard plots of Pb (II) adsorption onto PET-AA/AAM at 20°C.

The Redlich-Peterson isotherm constants, A , B , and g as well as the coefficient of determination, R^2 , for the sorption of Pb(II) on to PET-AA/AAM fiber using the linear regression is shown in Table I. It was observed that the coefficient of determination of Langmuir is higher than the other isotherms. It can be seen that the values of g were close to unity, which means that the isotherms are approaching the Langmuir form and not the Freundlich isotherm. The result shows that the Langmuir isotherm best-fit the equilibrium data for adsorption of Pb (II) on PET-AA/AAM fiber.

Scatchard analysis

Scatchard analysis was employed to further analyze the binding isotherms, which is an approximate model commonly used in SPE characterization. The Scatchard equation can be expressed as, $Q/C = (Q_{\max} - Q)/K_d$, where C ($\mu\text{mol mL}^{-1}$) is the equilibrium concentration of lead; Q ($\mu\text{mol g}^{-1}$) is the equilibrium adsorption amount at each concentration; Q_{\max} ($\mu\text{mol g}^{-1}$) is the maximum adsorption amount; and K_d ($\mu\text{mol mL}^{-1}$) is the equilibrium dissociation constant at binding sites. Figure 12 shows the Scatchard plots of the binding of lead to the resin. It is clear that the Scatchard plot for resin is a single straight line. The linear regression equation was $Q/C = -35.484Q + 7920.5$ ($R^2 = 0.9822$), suggesting that the homogeneous recognition sites for lead were formed in the SPE resin. From the slope $[-35.484 (1/K_d)]$ and intercept ($7920.5 (Q_{\max}/K_d)$), K_d and Q_{\max} for the affinity binding sites were calculated to be $0.028 \mu\text{mol mL}^{-1}$ and $221.8 \mu\text{mol g}^{-1}$, respectively.

Effect of foreign ions

To evaluate the selectivity of the preconcentration system, the effect of some metal ions (20 mg L^{-1}) on

the sorption behavior of Pb (II) ion (concentration 20 mg L^{-1}) was investigated. The extraction percentage ($E\%$) and the distribution ratio (D) were calculated from the following equations:

$$Q = (C_0 - C_e) V/W \quad (14)$$

$$E = (C_0 - C_e)/C_0 \quad (15)$$

$$D = Q/C_e \quad (16)$$

where Q represents the adsorption capacity (mg g^{-1}), C_0 and C_e represent the initial and equilibrium concentration of Pb(II) ($\mu\text{g mL}^{-1}$), W is the mass 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 Pb (II) on PET-AA/AAM fiber are Ag (I) and Fe (II). The effects of other mentioned foreign ions at given concentrations are negligible. The adsorption of Pb (II) on the PET-AA/AAM fiber in presence of all mentioned ions (with each ion having the concentration of 20 mg L^{-1}) shows that the Pb (II) can be determined quantitatively in the environmental samples.

Comparison with other methods

Comparative information from a number of studies on preconcentration of Pb (II) by various methods for the figure of merits is given in Table III. The sorption capacity and recovery of the present sorbent is superior in comparison with all the matrices shown in Table III. This new developed method has been successfully applied to the analysis of trace lead ions in natural water sample.

TABLE II
Effect of Other Ions on Sorption

Interfering	A	L (%)	E (%)	D
–	15.67	0	78.35	1.81
Co (II)	15.68	0	78.40	1.81
Ni (II)	15.14	3.4	75.70	1.56
Ba (II)	15.68	0	78.40	1.81
Hg (II)	15.70	0	78.50	1.82
Ag (I)	14.59	6.9	72.95	1.35
Fe (II)	14.18	9.5	70.9	1.22
Mg (II)	15.68	0	78.40	1.81
Cu (II)	15.67	0	78.35	1.81
Zn (II)	15.68	0	78.40	1.81
Ca (II)	15.69	0	78.45	1.82
K (I)	15.67	0	78.35	1.81
Mixed above ions	13.98	10.8	69.90	1.16

A , ions amount of adsorbed Pb(II) (mg L^{-1}), L , Loss adsorption (%), E , extraction percentage (%); and D , distribution ratio

TABLE III
Comparison of Recovery, Preconcentration, and Capacities with Some Literatures

Resin used	Recovery (%)	Preconcentration factor	Capacity (mg g ⁻¹)	Reference
Amberlite XAD-2 functionalized with o-aminophenol	91	40	3.32	27
Microcrystalline triphenylmethane loaded with quinolin-8-olate	98	100	–	28
Gallic acid-modified silica gel	96	25	12.63	29
Cellulose modified with triethylenetetramine	–	–	192.3	30
Sugarcane bagasse chemically modified with succinic anhydride	–	–	83.3	31
Chitosan modified ordered mesoporous silica	95	–	22.9	1
Macroporous epoxy resin-based polymer monolithic matrix	97	10	106.8	32
Thioureasulfonamide resin	97	2	0.5	33
Dibenzylthiocarbamate chelates on Dowex Optipore V-493	96	4–8	8.6	34
Amberlite XAD-2 with chromotropic acid	97	4–10	186.3	35
Amberlite XAD-2 with pyrocatechol	94	4–10	104.7	35
Amberlite XAD-2 with thiosalicylic acid	93	4–10	89.3	35
Amberlite XAD-7 with xylenol orange	91	4–10	16.9	35
PET-AA/AAm fiber (our resin)	100.2	10	44.1	–

Application of method

PET-AA/AAm fiber was used to preconcentrate and determine Pb (II) ions in The Persian Gulf (Boshehr, Nuclear Power Plant, Iran). The pH of water sample was adjusted to the optimum pH. Solid-phase extraction with PET-AA/AAm fiber coupled with FAAS was applied to determination of the Pb (II) in water sample. Since no Pb (II) was detected in the water sample, 100 mL water sample was spiked with 0.02, 0.04, and 0.06 mg of Pb (II) before subjecting it to the recommended procedure. The results are shown in Table IV. These results demonstrate the applicability of the procedure for Pb determination in samples with high recovery (>98%).

Determination of Pb (II) in plasma

Adsorption of Pb (II) ions on the PET-AA/AAm fiber from human serum was also studied in batch-wise. Human blood was collected from thoroughly controlled voluntary blood donors. Each unit separately controlled and found negative for HBS antigen and HIV I, II, and hepatitis C antibodies. No preservatives were added to the samples. Human blood was collected into EDTA containing vacutainers and red blood cells were separated from

plasma by centrifugation at 4000 × g for 30 min at room temperature, then filtered (3 μm Sartorius filter), and frozen at –20°C. Before use, the plasma was thawed for 1 h at 37°C. After no detection Pb (II) in the plasma, 25 mL plasma was spiked with 0.01 mg of Pb (II) before subjecting it to the recommended procedure. Then 25 mL volume of human serum containing 0.4 μg mL⁻¹ of Pb (II) ions were treated with 0.1 g of PET-AA/AAm fiber at room temperature and magnetically stirred at a speed of 600 rpm. After the desired treatment periods, the sorbent was taken out and sorbed metal ion was eluted with 0.5M nitric acid (10 mL). The concentration of the metal ion in the eluant was determined by FAAS. The experiments were performed in replicates of three. The results are shown in Table IV and indicate the suitability of the present sorbent for the preconcentration of lead from plasma samples. The similarity of results obtained by mentioned methods indicates that the reliability of the lead content data presented in Table IV is reasonable.

Analytical performance of the proposed system

Seven replicate determinations of 0.6 mg L⁻¹ lead solutions gave a relative standard deviation of 4.3%. The limit of detection corresponding to three

TABLE IV
Results Obtained for Pb (II) Determination in Plasma and Water
Sample of (I), (II), and (III)

Analyte	Plasma	(I)	(II)	(III)
Sample [without spiking of Pb (II)]	N.D.	N.D.	N.D.	N.D.
Added Pb (II) (μg mL ⁻¹)	0.4	0.2	0.4	0.6
Found Pb (II), after preconcentration (μg mL ⁻¹)	0.87	2.04	3.98	5.88
Preconcentration factor	2.5	10	10	10
Recovery %	87	100	99	98
Standard deviation	0.085	0.086	0.094	0.10
Relative standard deviation (%) ^a	6.5	4.2	2.4	1.8

^a For three determinations.

times the blank standard deviation was found to be $4.5 \mu\text{g L}^{-1}$. The limit of quantification corresponding to 10 times the blank standard deviation was found to be $15 \mu\text{g L}^{-1}$. The regression equation (after pre-concentration) was $A = 0.014C_{\text{Pb}} + 0.000$ ($R^2 = 0.9999$), and the conventional regression equation was $A = 0.004C_{\text{Pb}} + 0.000$ ($R^2 = 0.9957$). The enrichment factor, defined as the ratio of the slopes of the linear section of the calibration graphs before and after the preconcentration, was 3.5. The theoretical preconcentration factor, calculated as the ratio of the sample (100 mL) to the eluent volume (10 mL), was 10.

CONCLUSIONS

A new fibrous adsorbent was prepared by grafting acrylic acid/acryl amide comonomers onto poly (ethyleneterephthalate) fibers. The synthesis of the resin is simple and economical. The resin has a good potential for enrichment of trace amount of Pb (II) from large sample volumes. The resins also present 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 $44.05 \text{ (mg g}^{-1}\text{)}$ at 20°C . The R_L values showed that the PET-AA/AAM fiber was favorable for the adsorption of Pb (II). Pre-concentration by this resin combined with FAAS and ICP-AES can be applied to the determination of trace lead (II) ions in human plasma and water and the mineral reference sample with satisfactory results.

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