Full Length Research Paper

Determination and preconcentration of Mercury(II) from natural water and milk sample by Modified nano polyacrylonitrile fiber

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A simple method was developed for the preconcentration of Mercury(II) based on the adsorption of its Modified nano polyacrylonitrile fiber (PANF) complex. PANF was prepared by addition of acrylic fibers to ethanolamine (EA) with different concentration solutions. The stability of a chemically Modified nano polyacrylonitrile fiber were determined especially in concentrated hydrochloric acid which was then used as a recycling and preconcentration reagent for further uses of Modified nano polyacrylonitrile fiber. The application of this Modified nano polyacrylonitrile fiber for adsorption of a series of metal ions was performed by using different controlling factors such as the pH of metal ion solution and the equilibration shaking time by the static technique. Hg(II) was found to exhibit the highest affinity towards extraction by these Modified nano polyacrylonitrile fiber phases. The pronounced selectivity was also confirmed from the determined distribution coefficient (K_d) of all the metal ions, showing the highest value reported for Mercury(II) to occur by PANF. The potential applications of Modified nano polyacrylonitrile fiber for selective extraction of Mercury(II) to occur from aqueous solution were successfully accomplished as well as pre-concentration of low concentration of Hg(II) (40 pg ml-1) from natural tap water and milk sample with a pre-concentration factor of 200 for Hg(II) off-line analysis by cold vapor atomic absorption analysis. The preconcentration factor attainable for quantitative recovery (>96%) of Hg(II) was 100 for a 1000 mL sample volume.

Key words: Preconcentration, Mercury(II), Modified nano polyacrylonitrile fiber.

INTRODUCTION

Direct determination of trace metals especially toxic metal ions such as Mercury, Tin, lead and metalloids arsenic, Antimony and Selenium from various samples requires mostly an initial and efficient preconcentration step (Leyden et al., 1976). This preconcentration is required to meet the detection limits as well as to determine the lower concentration levels of the analyte of interest (Jones et al., 1983). This can be performed simply in many ways including liquid and solid phase extraction techniques (Nambiar et al., 1998; Caroli et al., 1991). The application of solid phase extraction technique for pre-concentration of trace metals from different samples results in several advantages such as the minimal waste generation, reduction of sample matrix effects as well as adsorption of the target species on the solid surface in a more stable chemical form (Alexandrova et al., 1993).

The normal and selective solid phase extractors are those derived from the immobilization of the organic compounds on the surface of solid supports which are mainly nano polyurethane forms (Arpadjan et al., 1997) , filter paper, cellulose (Gennaro et al., 1983) and ion exchange resins (Shamsipur et al., 2005). Silica gel, alumina, magnesia and zirconia are the major inorganic solid matrices used to immobilize the target organic modifiers on their surfaces (Unger, 1979) of which silica gel is the most widely used solid support due to the well documented thermal, chemical and mechanical stability properties compared to other organic and inorganic

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solid supports (Boudreau et al., 1989). The surface of silica gel is characterized by the presence of silanol groups, which are known as weak ion exchangers, causing low interaction, binding and extraction of the target analytes (Kvitek et al., 1982). For this reason, modification of the silica gel surface with certain functional groups has successfully been employed to produce the solid phase with certain selectivity characters (Bruening et al., 1991). Two approaches are known for loading the surface of solid phases with certain organic compounds and these are defined as the chemical immobilization which is based on chemical bond formation between the silica gel surface groups and those of the organic modifier, and the other approach is known as the physical adsorption in which direct adsorption of the organic modifier with the active silanol groups takes place (Unger, 1979).

Selective solid phase extractors and preconcentrators are mainly based on impregnation of the solid surface with certain donor atoms such as Oxygen, Nitrogen and Sulfur containing compounds (Mahmoud, 1999; Mahmoud and Soliman, 1997; Tong et al., 1990; Dadler et al., 1987). The most successful selective solid phases for soft metal ions are sulfur-containing compounds, which are widely used in different analytical fields. Amongst these sulfur-containing compounds are dithiocarbamate derivatives for selective extraction of Mercury(II) (Mahmoud, 1999, 1998) and preconcentration of various cations (Leyden et al., 1976; Moghimi et al., 2009; Tehrani et al., 2005) and 2-mercaptobenzothiazol-modified silica gel for on-line preconcentration and separation of silver for atomic absorption spectrometric determinations (Moghimi, 2006). Ammonium hexa-hydroazepin-1-dithiocarboxylate (HMDC)-loaded on silica gel as solid phase preconcentration column for atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) was reported (Alexandrova et al., 1993). Mercapto-modified silica gel phase was used in preconcentration of some trace metals from seawater (Moghimi et al., 2009). Sorption of Copper(II) by some sulfur-containing complexing agents loaded on various solid supports (Moghimi et al., 2011) was also reported. 2-Amino-1-cyclopentene-1-dithiocaboxylic acid (ACDA) for the extraction of Silver(I), Mercury(II), and Palladium(II) (Moghimi, 2006), 2-[2-triethoxysilyl-ethylthio] aniline for the selective extraction and separation of palladium from other interfering metal ions (Tehrani et al., 2005) as well as thiosemicarbazide for sorption of different metal ions (Moghimi et al., 2011) and thioanilide loaded on silica gel for preconcentration of palladium(II) from water (Tehrani et al., 2005) are also sulfur-containing silica gel phases.

Ion adsorption onto solid chelating nano polymer materials is now considered as one of the most promising techniques for selective concentration, removal and recovery of metal ions from a wide variety of sources. Among different types of polymer adsorbent, polymer fibers have attracted great interest in recent years (Tahaei et al., 2008). 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 (Abdouss et al., 2012).

Raw acrylic fibers (RAF), due to their chemical and thermal stability, are a good substrate for the modification. The mentioned advantages are mainly attributed to the high adsorption capacities, fast adsorption equilibrium, high recycling rate and low cost of these polymeric fibers. The use of commercial fiber and introducing functional groups on its structure are of the important methods for producing ion adsorbent fibers. The properties of the fiber can be maintained in this method (Abdouss et al., 2012).

In our previous attempts, we modified SPE membrane disks with suitable compounds for selective determination of Mercury (Ahmad et al., 2011; Tuzen and Soylak, 2005; Journal of Hazardous Materials, 2009). Meanwhile, other investigators have successfully utilized these sorbents for quantitative extraction and monitoring trace amounts of Lead (Tahaei et al., 2008).

This paper describes the applications of Modified nano polyacrylonitrile fiber (PANF) for selective extraction and solid phase preconcentration of Mercury(II) from aqueous and natural water samples.

EXPERIMENTAL

Reagents and materials

Analytical grade nitrate salts of Mercury, Manganese, Iron and Chromium litium, Sodium, Potassium, Magnesium, Calcium, Strontium, Barium, Zinc, Cadmium, Lead, Nickel, Cobalt(II) and Copper(II) of reagent grade were of the highest purity. Ultra pure organic solvents were obtained from Merck Chemical Company, Darmstat, Germany, and high purity deionized water was used throughout the experiments and 3-chloro propyl trimethoxysilane was received from Aldrich Chemical, USA. Organic solvents were dried according to conventional methods (Moghimi et al., 2009). For all solutions, double distilled water was used and the buffer solutions were prepared from 1.0 M sodium acetate to which different volumes of 1.0 M $HCl:HNO_3$ were mixed. It is obvious that pH should be adjusted by the use of a pH- meter.

Preparation of Modified nano polyacrylonitrile fiber (PANF)

PANF was prepared by adding 3 g of acrylic fibers to 300 ml of ethanolamine (EA) with different concentration solutions. The reaction mixtures were refluxed at 91°C under stirring for 2 h. The reaction product was cooled to room temperature, then the product was washed with acetone and distilled water and then air-dried. The content of the EA groups in the fiber was calculated as follows:

$$E_A = (W_1 - W_0)M_0 / (M_1 W_0)$$

(1)

Where EA is the content of EA groups in the fiber (mol/g), W_1 is the weight of the dry fiber after reaction (g), W_0 is the weight of the dry fiber before reaction (g), M_0 is the molecular weight chain unit CH_2CHCN, and M_1 is the molecular weight of $NH_2(CH_2)_2OH$ (Tabarzadi et al., 2010; Shin et al., 2004).

Activation of surface Modified nano polyacrylonitrile fiber (PANF) was filtered, washed with toluene, ethanol, and diethyl ether and was dried in an oven at 70°C for 6 h. 20.0 g of dry Modified nano polyacrylonitrile fiber (PANF). They filtered washed dried, three times the sample was filtered washed and dried. The phase was then dried in an oven at 60°C for 7 h.

Apparatus

The pH measurements were conducted by an ATC pH meter (EDT instruments, GP 353) calibrated against two standard buffer solutions of pH 4.0 and 9.2. Infrared spectra of PANF were carried out from KBr by a Perkin-Elmer 1430 ratio recording spectrophotometer. Atomic absorption analysis of all the metal ions except Mercury(II) were performed with a Perkin-Elmer 2380 flame AAS. Mercury(II) determinations were performed by a Varian Spect AA-10 plus atomic absorption spectrophotometer equipped with VGA-76 vapour generation

Electro spinning

The formation of a thin fiber via electrospinning is based on the uniaxial stretching (or elongation) of a viscoelastic jet derived from a polymer solution or melt (Nambiar et al., 1998). PAN is solved in common organic solvent (acetone). The solubility of raw acrylic fibers (RAF) in dimethylformamide (DMF) was (17:83 w/w) but it was observed that the solubility of PANF-EA was (19:81 w/w) and this is because of modification. The whole solutions were prepared by being dissolved in DMF (14:86 w/w) under stirring for several hours at room temperature. The aluminum plate were used as collector and prepared at 20630 cm^2. The polymer suspension was delivered to capillary nozzle via a feed line from a syringe pump. The spinneret protruded through the center of the plate. A power supply provided up to 20 kV to the plate and the distance between the capillary nozzle and the plate was adjusted at 20 cm to obtain a stable and continuous jet.

Adsorption and removed processes of metal ions

The adsorption ions onto PANF-EA for Nickel(II), Copper(II), and Lead(II) ions were investigated using the batch method. Experiments were carried out in an Erlenmeyer flask at the desired pH and 25°C temperature. The flasks were agitated on a shaker for 2 h. The amount of adsorbed metal was determined by the difference between the initial metal ion concentration and the final one after equilibrium (Nambiar et al., 1998). The concentration of ions was determined with a flame atomic absorption (FAA) spectrometer (Philips model PU9100).

The efficiency of metal ions recovery was estimated by the sorption yield (R%) and the q (mg/g) was calculated as:

$$R = (C_0 - C_t)/C_0 \times 100 \tag{2}$$

$$q = (C_0 - C_t)/G \times V \tag{3}$$

Where C_0 is the initial metal ion concentration (mg/l), C_t is the ion concentration after the adsorption period, V is the volume of solution L and G is the dry mass of the PANF-EA fiber sample (in grams). The metal ions adsorbed on the PANF-EA were then removed by placing 0.1 g of metal loaded fiber in 10 ml of 1 M HNO$_3$ solution for 30 min (Tahaei et al., 2008; Tuzen and Soylak, 2005).

Stability studies

The stability of PANF phases in different buffer solutions (pH 1 to 6) and concentrated hydrochloric and nitric acids were studied by batch equilibration. In this procedure, 500 mg of the phase was mixed with 50 ml of the selected solution in 100 ml measuring flask and automatically shaken for 5 h. The mixture was filtered, washed with 500 ml water and dried in an oven at 80°C. Around 100 mg of the treated phase was added to 1.0 ml of 0.1 M Mercury(II) and 9.0 ml of 0.1 M sodium acetate and the mixture was shaken for 30 min by an automatic shaker. The percentage of hydrolysis of polyacrylonitrile from the surface of PANF phases in different acidic solutions was calculated from the determined μmol g^{-1} value of each treated phase.

Sorption studies

Determination of metal capacity values (μmol g^{-1})

The determination of metal capacity of 13 metal ions, viz. Barium(II) Calcium(II), Cadmium(II), Cobalt(II), Cr(III), Copper(II), Iron(III), Mercury(II), Magnesium(II), Manganese(II), Nickel(II), Lead(II) and Zinc(II) as a function of pH was studied by the static technique. Then 100 mg of the dry phase was added to a mixture of 1.0 ml of 0.1 M metal ion and 9.0 ml of the buffer solution (pH 1 to 6 and 0.1 M sodium acetate) in 50 ml measuring flask. The mixture was then automatically shaken for 30 min, filtered, washed with 50 ml water and the unbound metal ion was subjected to complexometric titration using the proper buffer and indicator solutions and/or atomic absorption analysis. The effect of shaking time on the percentage extraction of metal ions was also studied for only Mercury(II) by the static technique. In this, 100 mg of the PANF phase was added to 1.0 ml of 0.1 M Mercury(II) and 9.0 ml of 0.1 M sodium acetate in 50 ml measuring flask and automatically shaken for the selected period of time (1, 5, 10, 20, 25, 30, and 35 min). The mixture was filtered, washed with 50 ml water and the free metal ion was determined as described above.

Determination of the distribution coefficient

About 100 mg of the PANF phase was mixed with 50 ml of the metal ion (1 mg.ml^{-1}) in a 100 ml measuring flask and shaken for 3 h by an automatic shaker. The mixture was filtered, washed with water and diluted with 2% nitric acid solution in order to fit in the linear dynamic range of each metal ion. A standard solution for each metal ion was also prepared in a similar way.

Percentage removal of Mercury(II) from aqueous solutions

One liter of Hg(II) solution, containing 10, 50 and 100 ng ml–1 was passed over a column (Mazlum et al., 2003) packed with 500 and 1000 mg each of Modified nano polyacrylonitrile fiber. The flow rate was adjusted to 2.0 ml min–1. The eluents were collected and 5ml was diluted with 20 ml of 2% nitric acid solution and subjected to cold vapor atomic absorption spectrometric analysis (CV-AAS).

Preconcentration of Mercury(II) from aqueous and natural tap water

Two liters (2 L) sample solution spiked with 20 pg ml^{-1} of Mercury(II) in both DDW and natural tap water were prepared and passed over a column packed with 1000 mg of PANF with a flow rate of 2 ml min^{-1}. Then 10 ml concentrated hydrochloric acid (10.0 M) was then
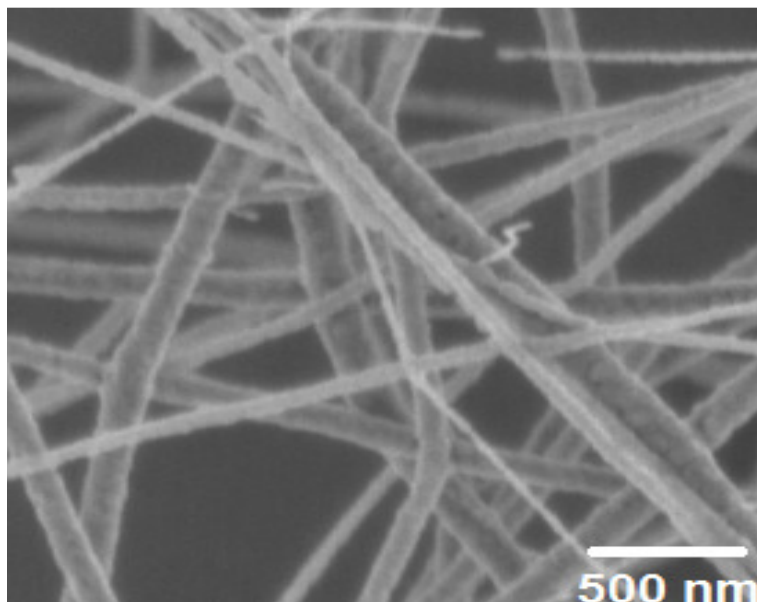
Figure 1. TEM images of the PET-AA/AAm fiber.

passed over the phase and adsorbed metal ion to desorb the bound-Mercury(II). The desorbed metal ion was directly determined by CV-AAS. A standard solution and blank aqueous and tap water samples were also prepared and determined for evaluation.

RESULTS AND DISCUSSION

Figure 1 shows transmission electron microscopy (TEM) images of the PANF. The fibers are approximately 100 to 200 nanometers in diameter. As the fibers themselves have a small diameter, the thickness of the nano web can likewise be quite small. The thin nano web has limited mechanical properties that preclude the use of conventional web handling and filter pleating equipment. As a result, nano fiber webs have been applied onto various substrates. Substrates are selected to provide appropriate mechanical properties to allow pleating, filter fabrication, durability in use, and in some cases, filter cleaning. Usually, substrates are often chosen to resemble conventional filter materials, which allow the use of conventional filter media pleating and element handling equipment.

Stability studies

The stability of the newly synthesized Modified nano polyacrylonitrile fiber phases was performed in different buffer solutions (pH 1, 2, 3, 4, 5, 6 and 0.1M sodium acetate) in order to assess the possible leaching or hydrolysis processes. Because the metal capacity values determined in Section 3.2 revealed that the highest one corresponds to Hg(II), this ion was used to evaluate the stability measurements for the Modified nano polyacrylonitrile fiber phase (Mahmoud, 1979). The results of this study proved that the Modified nano polyacrylonitrile fiber is more resistant than the chemically adsorbed analog especially in 1.0, 5.0 and 10.0M hydrochloric acid with hydrolysis percentage of 2.25, 6.10 and 10.50 for phase, respectively.

However, the use of nitric acid with different concentration values (1.0, 5.0, 10.0 M) was found to change the color of Modified nano polyacrylonitrile fiber from dark brown into reddish brown which is interpreted on the basis of chemical changes of the organic nano polyacrylonitrile modifier via oxidation. In addition, stability of phases was also confirmed from the interaction with 10.0M hydrochloric acid for more than 1 week.

This test proved a reasonable stability of Modified nano polyacrylonitrile fiber phase compared to non-treated silica gel phases judging from the color change of the two phases as well as the metal capacity values determination of Hg(II) and comparison of these with those of the original non-treated Modified nano polyacrylonitrile fiber phases.

Thus, these stability studies indicated the suitability of phase for application in various acid solutions especially concentrated hydrochloric acid and extension of the experimental range to very strong acidic media which is not suitable for other normal and selective chelating ion exchangers based on a nano polymeric matrix (Shamsipur et al., 2005; Tuzen et al., 2009; Gode and Pehlivan, 2005). Finally, the Modified nano polyacrylonitrile fiber phases were also found to be stable over a range of one year during the course of this work.

Table 1. Metal capacity values determined in µmol g^{-1a}.

pH	Mercury(II)	Lead(II)	Chromium (II)	Manganese(II)	Iron(II)	Cobalt(II)	Nickel(II)	Copper(II)	Zinc(II)	Cadmium (II)	Calcium	Magnesium	Barium
1	10	3	3	13	6	5	14	14	00	00	2	00	2
2	22	7	8	18	26	10	25	25	00	5	15	5	6
3	39	12	10	28	30	14	38	45	5	16	25	10	13
4	58	25	15	50	44	25	38	60	10	25	30	15	20
5	137	33	23	69	10	50	69	75	20	39	35	29	29
6	210	45	36	58	-	35	64	91	39	68	21	28	38
NaOAc	240	59	52	20	-	14	43	63	19	40	23	20	30

[a] Values are based on n = 3 with standard deviation of 4.

Metal capacity in various controlling factors

The metal capacity values determined in µmol g–1 for the Modified nano polyacrylonitrile fiber in different buffer solutions were studied to evaluate the pH effect of metal ion on the extractability of the Modified nano polyacrylonitrile fiber phase. Table 1 compiles the µmol g–1 values for the 13 tested metal ions, viz) Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II),Cd(II),Ca, Mg, Ba, Pb(II) and Hg(II).s Several trends can be observed and outlined from the data given. First, is the strong dependence of µmol g–1 extracted values from the metal ion solution for most tested metal ions on the pH-value (Moghimi et al., 2009).

The maximum value was found to be mainly at higher pH-values (pH 5–6 and 0.10M NaOAc). Second, is the strong affinity of the Modified nano polyacrylonitrile fiber phase for extraction and removal of Hg(II) from aqueous solution compared to other tested metal ions, as shown by the higher µmol g–1 values by Modified nano polyacrylonitrile fiber phases(Moghimi et al., 2009).

This behavior of Modified nano polyacrylonitrile fiber –loaded sulfur -containings compounds for selective extraction and removal of Hg(II) from aqueous and natural water sample is well documented (Mahmoud, 1999, 1998) and reported based on different governing rules (Tong et al.1990) Third are the notably high µmol g–1 values determined for chemically Modified nano polyacrylonitrile fiber phase in comparison with values found as given in Table 1. The comparison between the metal sorption properties of chemically and physically- Modified nano polyacrylonitrile fiber phases has been extensively studied (Leyden et al., 1976) and the results presented in this work are consistent with the surface activity of the donor atoms responsible for metal ion interaction, sorption, extraction and selective removal. In the case of the physically adsorbed phase, some of these donor atoms are involved in physical adsorption processes with the active surface, leading to the minimization of the reactivity of such donor atoms for metal interaction and binding processes. The product, Modified nano polyacrylonitrile fiber, in this case is tuned with the active donor atoms (N) directed with the capability and accessibility for fast and direct interactions with the free metal ion present in solution. Fourth, are the general orders of metal capacity values for all tested metal ions by the two phases which are in many respects consistent and similar. Therefore, the conclusion drawn from this section can be outlined as the high superiority of phase for selective extraction of Hg(II) as well as the higher metal uptake behavior of Modified nano polyacrylonitrile fiber phase .

The effect of shaking time on the percentage extraction of metal ions at various equilibration time intervals (1, 5, 10, 15, 20, 25 min) was also studied and evaluated as µmol g–1 and correlated to that determined at 30 min shaking time. Figure 2 represents the percentage extraction versus shaking time in minute and clearly reflects the rapid exchange equilibrium between Modified nano polyacrylonitrile fiber phase and Hg(II). One-minute shaking time was found to be sufficient to establish 84% of the determined µmol g–1 value at 30 min whereas 10 min shaking time led to 88% extraction. Modified nano polyacrylonitrile fiber phase as previously declared in the stability studies.

The distribution coefficient (Kd) data of the tested metal ions with the boths newly Modified polyacrylonitrile fiber phases are summarized in Table 2. It is evident that Hg(II) is the strongest sorbed metal ion by Modified nano polyacrylonitrile fiber phase. The distribution coefficient values of Hg(II) by the loaded Modified nano polyacrylonitrile fiber phase were found to be much higher than those reported for ion exchange resins containing Modified nano
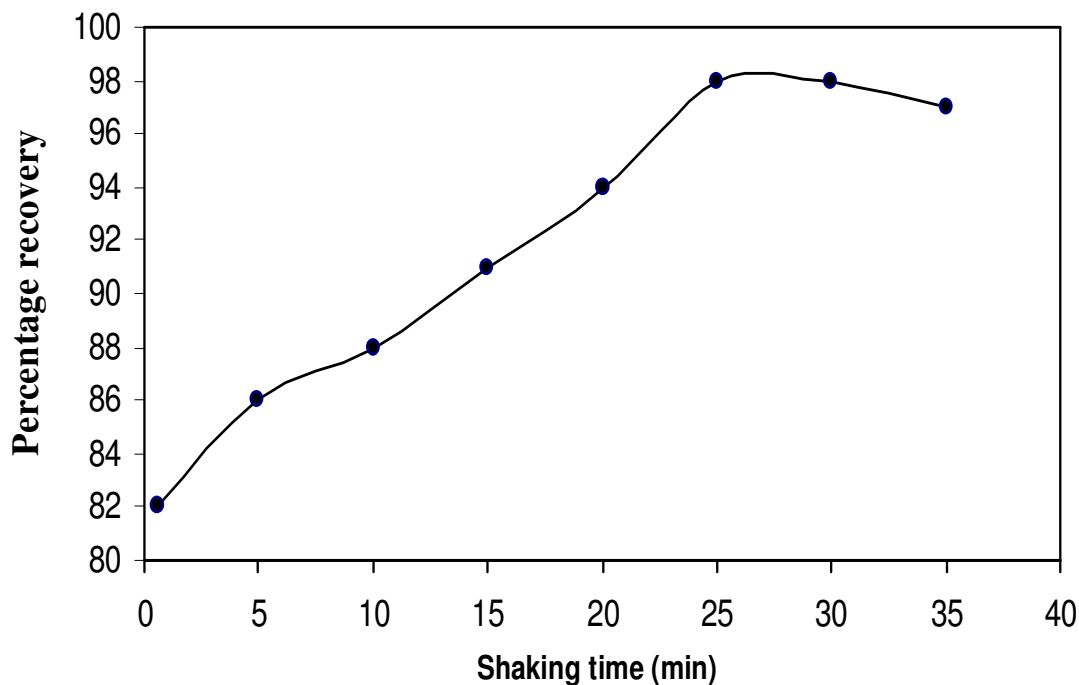
Figure 2. Effect of shaking time (min) on the percentage extraction of Mercury(II) by the PANF phases.

Table 2. Distribution coefficient (K_d) values of various metal ions.

Metal ion	Distribution coefficient (K_d)
Chromium(III)	190
Manganese(II)	98
Iron(III)	78
Cobalt(II)	70
Nickel(II)	60
Copper(II)	760
Zinc(II)	445
Cadmium(II)	115
Mercury(II)	12000
Lead(II)	190

polyacrylonitrile fiber derivatives (Shamsipur et al., 2005). In addition, the Kd values for Cu(II) by Modified nano polyacrylonitrile fiber phase were found to come on the second place after Hg(II) which behavior can be interpreted on the basis of the affinity of both nitrogen and hidroxyl donor groups present in Modified nano polyacrylonitrile fiber for binding with Cu(II) (Mahmoud, 1999, 1998). On the other hand, the various tested metal ions as shown in Table 2 were found to exhibit lower tendency to bind with Modified nano polyacrylonitrile fiber phase judging from the comparable low distribution coefficient values determined for these metal ions. The higher Kd value for Hg(II) and the lower ones for the other metal ions, except Cu(II), provide an additional evidence for the suitability of these two newly Modified nano polyacrylonitrile fiber phase for selective extraction of Hg(II) from aqueous solutions. It is also noteworthy that the conclusion drawn from the evaluation of the Kd values by Modified nano polyacrylonitrile fiber phase is consistent with the reported data.

Percentage removal of Hg(II) from aqueous solution

The use of a column technique is a common procedure for extraction, separation and selective extraction of

Table 3. Percentage removal of Mercury(II) from aqueous solutions by PANF phase[a].

Mercury(II) spiked (ng ml^{-1})	Phase (mg)	Percentage removal
10	500	94 ± 1.5
50	500	96 ± 3
100	500	94 ± 6
10	1000	99 ± 5
50	1000	98 ± 2
100	1000	98 ± 3

[a]Values are based on triplicate analysis.
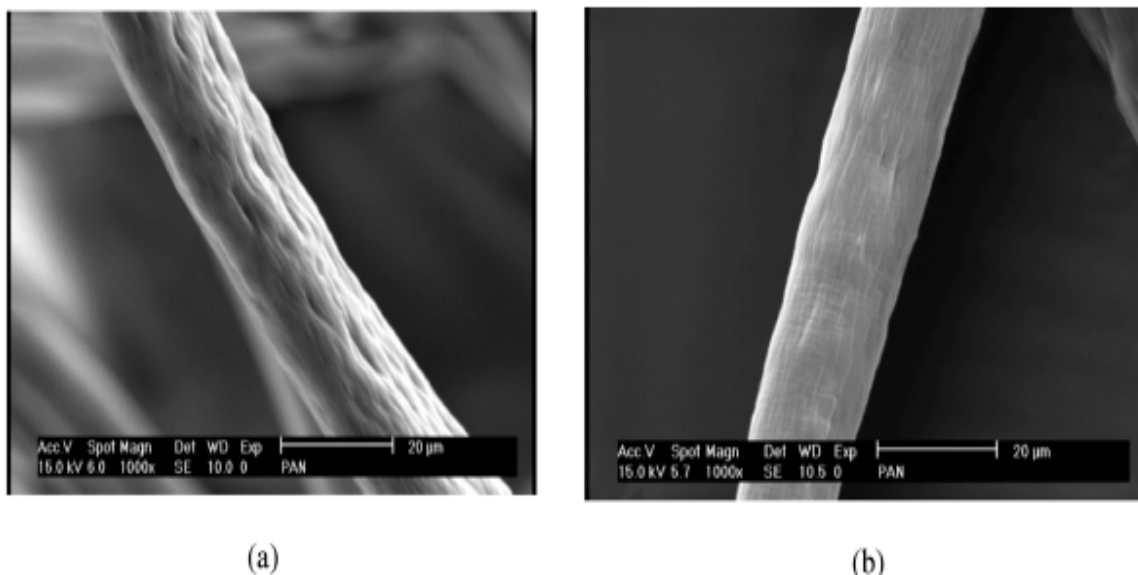
Figure 3. SEM image of (a) the raw fiber and (b) modified PAN fiber.

metal ions from various aquatic systems (Unger, 1979). The column technique is characterized by major advantages over the batch or static equilibration method that is the possible application to large sample volumes (Mahmoud, 1999; Mahmoud, 1997; Tong et al., 1990; Dadler et al., 1987). This property enables the pre-concentration of metal ions at very low trace levels. The percentage removal of metal ions from aqueous solutions is essential for the evaluation of the method described and suggested here. This is mainly dependent on several well known factors such as the type and amount of packing stationary and mobile phases and the flow rate of the mobile phase (Leyden et al., 1976). In this study, we attempted to evaluate the percentage recovery of Hg(II) with different spiked concentrations, namely 10, 50 and 100 ng ml–1 from 1 l of 0.1M NaOAc solution by the application of two different amounts (500 and 1000 mg) of Modified nano polyacrylonitrile fiber phase packing. The results of the percentage removal of Hg(II) from aqueous solutions are presented in Table 3 which clearly

demonstrate the suitability and validity of Modified nano polyacrylonitrile fiber phase for removal and extraction of Hg(II). In addition, the effect of packing amount of silica gel phase is also evident in Table 3, where the near completion of Hg(II) removal was accomplished by the use of 1000 mg phase.

SEM investigations

Scanning electron microscopy (SEM) was used to examine the external surface of the fiber before and after modification. As can be seen from Figure 3, original acrylic fiber comparatively surface (Figure 3(a)), and with modified fiber (PANF-EA), obvious change comparing to that of the RAF fiber was observed (Figure 3(b). It is clear that changes have occurred in the morphology of the fiber but photographs demonstrated that the surface of PANF-EA was approximately as smooth, swollen and homogeneous as that of the raw fiber. This can be
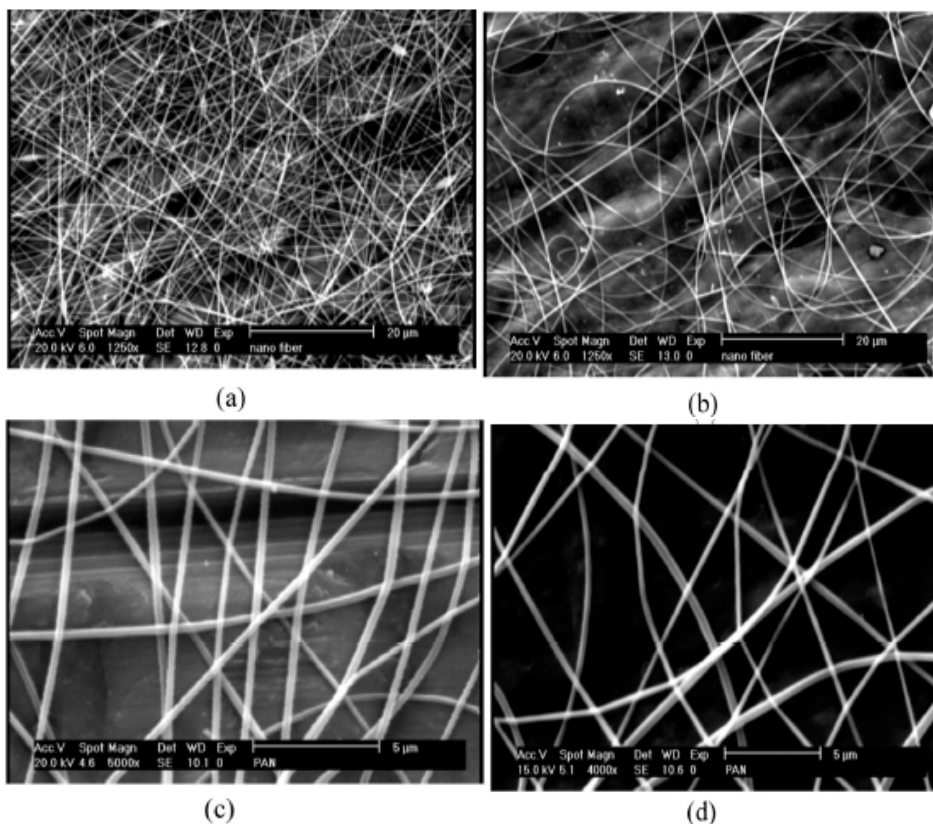
Figure 4. SEM image of (a)(c) the raw nano fiber and (b)(d) modified PAN nano fiber.

related to new functional groups that were bigger than CN groups.

Scanning electron microscopy (SEM) was so used to examine the morphology of the nano fiber before and after modification. As shown in Figure 4, original acrylic nano fiber comparatively morphology (Figure 4a), and with Modified nano fiber (PAN-EA), obvious change compared to that of the raw fiber was observed (Figure 4b). The Modified nano fiber was roundelay as that of raw acrylic nano fiber. This can be related to modification treatment and incorporation of new functional groups into the fiber structure.

Selective pre-concentration of Hg(II) from natural water for off-line CV-AAS

This study was undertaken in order to evaluate the potential application of Modified nano polyacrylonitrile fiber phase for pre-concentration of trace levels of Hg(II) in natural water samples. Drinking tap water was used without prior treatments as an example and compared with double distilled water (DDW) to evaluate and investigate the matrix effect. Both drinking tap water and DDW(2 l) were spiked with 20 pg ml–1 of Hg(II). Several pre-concentration reagents are well known and extensively examined for desorption of the bound metal ions from the surface of the stationary phase and these include mainly, hydrochloric and nitric acid, thiourea HCl (Shamsipur et al., 2005). as well as ethylenediaminetetraacetic acid (Moghimi et al., 2009). However, some of these reagents are usually characterized by adsorption on the surface of Modified nano polyacrylonitrile fiber which leads to severe change in the nature of packing material as well as non reproducible results if the column used in future applications. The efficiency of metal ion pre-concentration especially Hg(II), by 10.0M HCl acid is found to be high without causing any notable change to the chemical nature of the organic Modified nano polyacrylonitrile fiber. Therefore, 10.0 ml of 10.0M HCl was used for the elution of the adsorbed Hg(II) from the column bed. The pre-concentration factor targeted from this study is 200 as given in Table 4. As the results indicate, the off-line detection results of the eluted and pre-concentrated Hg(II) are very good with a satisfactory pre-concentration factor which can be further increased to 500-fold by simply increasing the water sample volume to 5 l instead of 2 l. Moreover, natural tap water sample was found to give very close results to that reported for DDW sample and this comparison indicates that the matrix effects of the dissolved inorganic and organic matters played an insignificant role in the aimed

Table 4. Preconcentration of Mercury(II) from DDW and natural tap water samples[a].

Phase (mg)	Sample Volume (ml)	Hg(II)spiked (pg ml^{-1})	Preconcentration reagent	Preconcentration factor	Mercury(II) detected[a] (ng ml^{-1})	Percentage removal
1000	2000 Tap water (Saveh)	20	10.0 ml of 10.0 M HCl	200	3.96 ± 2.0	99.6 ± 1.7
1000	2000 DDW	20	10.0 ml of 10.0 M HCl	200	3.94 ± 2.1	98.4 ± 1.9
1000	2000 milk	20	10.0 ml of 10.0 M HCl	200	3.62 ± 2.7	97.35 ± 1.6

[a] Values are corrected for blank concentration of water samples and based on triplicate analysis.
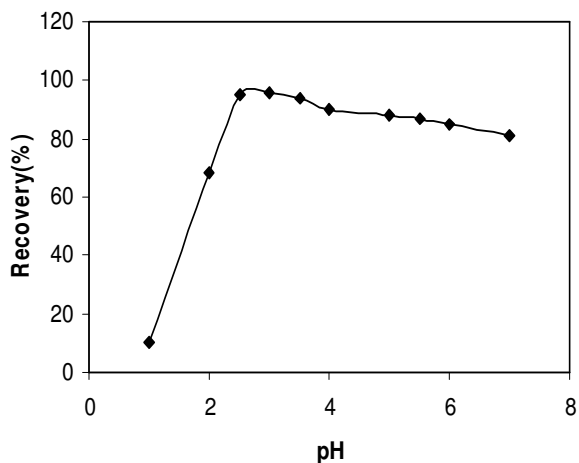
Figure 5. Effect of pH sorption of Mercury(II) onto PANF. Shaking time, 5 h; Temperature, 25°C.

selective extraction, removal and pre-concentration of Hg(II) by Modified nano polyacrylonitrile fiber phase.

Effect of pH

According to the recommended procedure solutions (the volume of each 100 ml) containing 0.51 g ml^{-1} of Mercury(II) was taken. Their pH values were adjusted in range of 1.5 to 7 with HNO_3, 0.01 M acetate and/or phosphate buffer solutions and the mixture was shaken for 5 h. Hg (II) was determined by the 0.1 g of Modified nano polyacrylonitrile fiber in different pH value, namely pH 1.5, 2, 3, 4, 5, 6, and 7. It also can be seen in Figure 5, the sorption quantity of Hg (II) increases with the pH value increases in the studied pH ranges. Below pH 2.0, the sorption quantity of Nickel (II) is very low since the functional groups were protonated. Owing to hydrolysis at higher pH value, pH 2.8 was chosen as the optimum pH for further studies.

Conclusions

Thus a selective and sensitive method for the determination of trace levels of Hg (II) based on Modified

nano polyacrylonitrile fiber as a sorbent for the determination of the analytes in milk sample as well as natural water samples. The sorption capacity for Hg (II) is 44.01 mg g–1 that is higher than most of the sorbents (Ahmad et al., 2011).The faster sorption and desorption are other distinct advantages. In comparison to the commonly immobilized in silica gel, the present sorbent has a superior preconcentration factor (100-folds) for Hg (II) (Abdouss et al., 2012; Ahmad et al., 2011).

In addition, the preparation of Modified nano polyacrylonitrile fiber is relatively simple and rapid. But the Modified nano polyacrylonitrile fiber sorbent has some drawbacks such as lower reusability and stability, which can be repeated to use 10 cycles. This may make it difficult to put into practical use and should be a subject of further investigations.

Results presented in this work demonstrate well the tremendous possibilities offered by the solid phase extraction of trace amounts of Hg(II) in water samples its determination by cold vapor atomic absorption analysis. The method developed was simple, reliable, and precise for determining Hg (II) in water. Also, the proposed method was free of interference compared to conventional procedures to determine Hg (II) (Choi and Choi, 2003; Moghimi et al., 2009; Tuzen et al., 2009). The method can be successfully applied to the separation and determination of Hg (II) in binary mixtures.

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