



ISSN: 0973-4945; CODEN ECJHAO
E-Journal of Chemistry
2011, 8(3), 1052-1061

Preconcentration of Cr(III) from Natural Water by Modified Nano Polyacrylonitrile Fiber by Methanolamine

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Received 15 December 2010; Accepted 24 January 2011

Abstract: Modified nano polyacrylonitrile fiber (PANF) was prepared by adding acrylic fibers to methanolamine (MMA) with different concentration solutions. The stability of a chemically modified nano polyacrylonitrile fiber especially in concentrated hydrochloric acid which was then used as a recycling and pre-concentration reagent for further uses of modified nano polyacrylonitrile fiber. The application of this modified nano polyacrylonitrile fiber for sorption 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. Cr(III) 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 Cr(III) to occur by modified nano polyacrylonitrile fiber. The modified nano polyacrylonitrile fiber for selective extraction of Cr(III) were successfully accomplished in aqueous solution as well as preconcentration of low concentration of Cr(III) (60 pg mL^{-1}) from natural tap water with a preconcentration factor of 100 for Cr(III) and then off-line Cr(III) in water samples were determined by flame atomic absorption.

Keywords: Preconcentration, Cr(III), Modified nano polyacrylonitrile fiber, Methanolamine

Introduction

Toxicological studies have proved that the degree of toxicity of an element directly depends on the species in which it is present. Cr(III) is considered as an essential micronutrient for humans and mammals in order to maintain glucose metabolism, where as Cr(VI) is a potentially carcinogenic agent¹. The significant drawbacks of Cr(VI) are breathing disturbances, liver and digestion malfunctions, dermal corrosion and skin allergies².

Therefore, it is necessary to control the level of chromium in industrial effluent, natural and drinking waters. Speciation of chromium in environmental samples is of prime importance.

Therefore there are numerous methods and techniques concerning chromium speciation and determination including liquid-liquid extraction after complex formation³⁻⁴, solid-liquid extraction⁵⁻⁸, LC-AAS⁹⁻¹¹, spectrophotometric¹², ICP-AES¹³ and NAA¹⁴. However, some of these techniques are currently, time consuming and have elaborate sample preparation steps and low enrichment factors.

Solid phase extraction (SPE) methods are the best alternatives for traditional classic methods due to selective removal of trace amounts of metal ions from their matrices. SPE determinations can be carried out on different efficient ways. One of the most appropriate performance features of SPE is achieved by using octadecyl silica membrane disks. SPE reduce the use of toxic solvent, disposal costs, and extraction time¹⁵⁻¹⁶. The octadecyl silica membrane disks involves shorter sample processing time and decreased plugging due to the large cross-sectional area of the disk and small pressure drop which allows higher flow-rates; reduced channeling resulting from the use of sorbent with smaller particle size and a greater mechanical stability of the sorbent bed¹⁷.

In our previous attempts, we modified SPE membrane disks with suitable compounds for selective determination of chromium¹⁸⁻¹⁹ and lead²⁰. Meanwhile, other investigators have successfully utilized these sorbents for quantitative extraction and monitoring trace amounts of lead²¹⁻²³, copper²⁴⁻²⁶, silver²⁷⁻²⁸, mercury²⁹⁻³⁰, cadmium³¹, palladium³², Ce³³ and UO₂³².

This paper describes the applications of modified nano polyacrylonitrile fiber for selective extraction and solid phase preconcentration of Cr(III) from aqueous and natural water samples.

Experimental

Analytical grade nitrate salts of Hg, Mn, Fe and Cr lithium, 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 E.Merck, 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. 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; HNO₃ were mixed and the pH-value of the resulting solution was adjusted with the use of a pH- meter.

Preparation of modified nano polyacrylonitrile fiber

Modified nano polyacrylonitrile fiber was prepared by adding 3 g of acrylic fibers to 300 mL of methanolamine (MMA) 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 MMA groups in the fiber was calculated as follows:

$$E_A = (W_1 - W_0)M_0 / (M_1 W_0) \quad (1)$$

Where EA is the content of MMA groups in the fiber (mol/g), W₁ is the weight of the dry fiber after reaction (g), W₀ is the weight of the dry fiber before reaction (g), M₀ is the molecular weight chain unit CH₂CHCN(53) and M₁ is the molecular weight of NH₂(CH₂)₂OH^{31,32}.

Activation of surface modified nano polyacrylonitrile fiber (PANF) was filtered, washed with toluene, methanol and diethyl ether and dried in an oven at 70 °C for 6 h. An amount of 20.0 g of dry Modified nano polyacrylonitrile fiber (PANF) .The resulting phase was filtered, washed with toluene, methanol and finally with water several times. 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 modified nano polyacrylonitrile fiber (PANF) were carried out from KBr by a Perkin-Elmer 1430 ratio recording spectrophotometer. Atomic absorption analysis of all the metal ions except Cr(III) were performed with a Perkin-Elmer 2380 flame atomic absorption spectrometer. Cr(III) 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 melt³. PAN is solved in common organic solvent. The solubility of raw acrylic fibers (RAF) in dimethylformamide (DMF) was 17:83w/w, but it was observed that the solubility of PANF-MMA was 19:81w/w and this is because of modification. The whole solutions were prepared by being dissolved in DMF (14:86w/w) under stirring for several hours at room temperature. The aluminum plate were used as collector and prepared at 20630 cm². 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-MMA for Ni (II), Cu (II) and Pb(II) ions were investigated using the batch method. Experiments were carried out in an Erlenmeyer flask at the desired pH and 25°C temperatures. 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 equilibrium³. 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:

$$R = (C_0 - C_t) / C_0 \times 100 \quad (2)$$

$$q = (C_0 - C_t) / G \times V \quad (3)$$

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-MMA fiber sample (in g). The metal ions adsorbed on the PANF-MMA were then removed by placing 0.1 g of metal loaded fiber in 10 mL of 1M HNO₃ solution for 30 minutes²⁸.

Stability studies

The stability of modified nano polyacrylonitrile fiber phases in different buffer solutions (pH 1–6) and concentrated hydrochloric and nitric acids was 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 Cr(III) 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 modified nano polyacrylonitrile fiber phases in different acidic solutions was calculated from the determined ($\mu\text{mol g}^{-1}$) value of each treated phase.

Sorption studies

Determination of metal capacity values ($\mu\text{mol g}^{-1}$)

The determination of metal capacity of 13 metal ions, viz. Ba(II), Ca(II), Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Hg(II), Mg(II), Mn(II), Ni(II), Pb(II) and Zn(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 1-6 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 Cr(III) by the static technique. In this, 100 mg of the modified nano polyacrylonitrile fiber phase was added to 1.0 mL of 0.1 M Cr(III) 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 modified nano polyacrylonitrile fiber 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 Cr(III) from aqueous solutions

One liter of Cr(III) solution, containing 10, 50 and 100 ng mL^{-1} was passed over a column²⁷ 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 5 mL was diluted with 20 mL of 2% nitric acid solution and subjected to flame atomic absorption spectrometric analysis (FAAS).

Preconcentration of Cr(III) from aqueous and natural tap water

Two liters sample solution spiked with 20 pg mL^{-1} of Cr(III) in both double distilled water (DDW) and natural tap water were prepared and passed over a column packed with 1000 mg of modified nano polyacrylonitrile fiber with a flow rate of 2 mL min^{-1} . Then 10 mL concentrated hydrochloric acid (10.0 M) was then passed over the phase and adsorbed metal ion to desorb the bound-Cr(III). The desorbed metal ion was directly determined by FAAS. A standard solution and blank aqueous and tap water samples were also prepared and determined for evaluation.

Results and Discussion

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 0.1 M sodium acetate) in order to assess the possible leaching or hydrolysis processes. Because the metal capacity values revealed that the highest one corresponds to Cr(III), ion was used to evaluate the stability measurements for the modified nano polyacrylonitrile fiber phase¹⁴. 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 10.0 M 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 and 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 10.0 M 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 Cr(III) 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 matrix⁹. Finally, the modified nano polyacrylonitrile fiber phases were also found to be stable over a range of 1 year during the course of this work.

Metal capacity in various controlling factors

The metal capacity values determined in $\mu\text{ mol g}^{-1}$ 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 shows that the $\mu\text{ mol g}^{-1}$ values for the 13 tested metal ions, viz. Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Cr(III) and Pb(II). Several trends can be observed and outlined from the data given. First, is the strong dependence of $\mu\text{ mol g}^{-1}$ extracted values from the metal ion solution for most tested metal ions on the pH-value^{20,25}.

Table 1. Metal capacity values determined in $\mu\text{ mol g}^{-1a}$

| pH | Cr(III) | Pb(II) | Hg(II) | Mn(II) | Fe(III) | Co(II) | Ni(II) | Cu(II) | Zn(II) | Cd(II) | Ca | Mg | Ba |
|-------|---------|--------|--------|--------|---------|--------|--------|--------|--------|--------|----|----|----|
| NaOAc | 240 | 59 | 52 | 20 | - | 14 | 43 | 63 | 19 | 40 | 23 | 20 | 30 |
| 6 | 210 | 45 | 36 | 58 | - | 35 | 64 | 91 | 39 | 68 | 21 | 28 | 38 |
| 5 | 137 | 33 | 23 | 69 | 10 | 50 | 69 | 75 | 20 | 39 | 35 | 29 | 29 |
| 4 | 58 | 25 | 15 | 50 | 44 | 25 | 38 | 60 | 10 | 25 | 30 | 15 | 20 |
| 3 | 39 | 12 | 10 | 28 | 30 | 14 | 38 | 45 | 5 | 16 | 25 | 10 | 13 |
| 2 | 22 | 7 | 8 | 18 | 26 | 10 | 25 | 25 | 00 | 5 | 15 | 5 | 6 |
| 1 | 10 | 3 | 3 | 13 | 6 | 5 | 14 | 14 | 00 | 00 | 2 | 00 | 2 |

^a Values are based on $n=3$ with standard deviation of 4

The maximum value was found to be mainly at higher pH-values (pH 5–6 and 0.10 M NaOAc). Second, is the strong affinity of the modified nano polyacrylonitrile fiber phase for extraction and removal of Cr(III) from aqueous solution compared to other tested metal ions, as shown by the higher $\mu\text{ mol g}^{-1}$ values by modified nano polyacrylonitrile fiber phases²⁵.

This behavior of modified nano polyacrylonitrile fiber loaded sulfur containing compounds for selective extraction and removal of Cr(III) from aqueous and natural water sample is well documented^{19,20} and reported based on different governing rules¹⁷. Third are the notably high $\mu\text{ mol g}^{-1}$ 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 studied²¹ 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 Cr(III) 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 and 25 min) was also studied and evaluated as $\mu\text{ mol g}^{-1}$ and correlated to that determined at 30 min shaking time. Figure 1 represents the percentage extraction versus shaking time in min and clearly reflects the rapid exchange equilibrium between modified nano polyacrylonitrile fiber phase and Cr(III). One minute shaking time was found to be sufficient to establish 84% of the determined $\mu\text{ mol g}^{-1}$ value at 30 min whereas 10 min shaking time led to 88% extraction. The data and results presented in this section reveal the superiority of modified nano polyacrylonitrile fiber phase as previously declared in the stability studies.

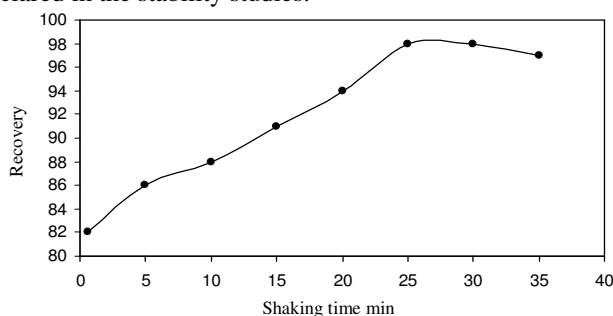


Figure 1. Effect of shaking time (min) on the percentage extraction of Cr(III) by the modified nano polyacrylonitrile fiber phases

The distribution coefficient (K_d) data of the tested metal ions with the two newly modified polyacrylonitrile fiber phase are summarized in Table 2. It is evident that Cr(III) is the strongest sorbed metal ion by modified nano polyacrylonitrile fiber phase. The distribution coefficient values of Cr(III) by the loaded modified nano polyacrylonitrile fiber phase were found to be much higher than those reported for ion exchange resins containing modified nano polyacrylonitrile fiber derivatives⁹. In addition, the K_d values for Cu(II) by modified nano polyacrylonitrile fiber phase were found to come on the second place after Cr(III)

which behavior can be interpreted on the basis of the affinity of both nitrogen and hydroxyl donor groups present in modified nano polyacrylonitrile fiber for binding with Cu(II)^{19,20}. 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 K_d value for Cr(III) 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 Cr(III) from aqueous solutions. It is also noteworthy that the conclusion drawn from the evaluation of the K_d values by modified nano polyacrylonitrile fiber phase is consistent with the reported data.

Percentage removal of Cr(III) from aqueous solution

The use of a column technique is a common procedure for extraction, separation and selective extraction of metal ions from various aquatic systems¹⁰. The column technique is characterized by major advantages over the batch or static equilibration method that is the possible application to large sample volumes¹⁴⁻¹⁶. This property enables the preconcentration 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 phase²¹. In this study, we attempted to evaluate the percentage recovery of Cr(III) with different spiked concentrations, namely 10, 50 and 100 ng mL⁻¹ from 1 l of 0.1 M 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 Cr(III) 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 Cr(III). In addition, the effect of packing amount of silica gel phase is also evident in Table 3, where the near completion of Cr(III) removal was accomplished by the use of 1000 mg phase.

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

| Metal ions | K_d |
|------------|-------|
| Cr(III) | 240 |
| Mn(II) | 89 |
| Fe(III) | 77 |
| Co(II) | 76 |
| Ni(II) | 65 |
| Cu(II) | 700 |
| Zn(II) | 499 |
| Cd(II) | 118 |
| Cr(III) | 12600 |
| Pb(II) | 130 |

Table 3. Percentage removal of Cr(III) from aqueous solutions by modified nano polyacrylonitrile fiber phase^a

| Cr(III) spiked, ng mL ⁻¹ | Phase, mg | Percentage removal |
|-------------------------------------|-----------|--------------------|
| 10 | 500 | 94±4 |
| 50 | 500 | 96±4 |
| 100 | 500 | 97±3 |
| 10 | 1000 | 99±3 |
| 50 | 1000 | 95±2 |
| 100 | 1000 | 96±4 |

^a Values are based on triplicate analysis

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 2, original acrylic fiber comparatively surface (Figure 2(a)) and with modified fiber (PANF-MMA), obvious change

comparing to that of the RAF fiber was observed (Figure 2(b)). It is clear that changes have occurred in the morphology of the fiber but photographs demonstrated that the surface of PANF-MMA was approximately as smooth, swollen and homogeneous as that of the raw fiber. This can be related to new functional groups that were bigger than (CN) groups.

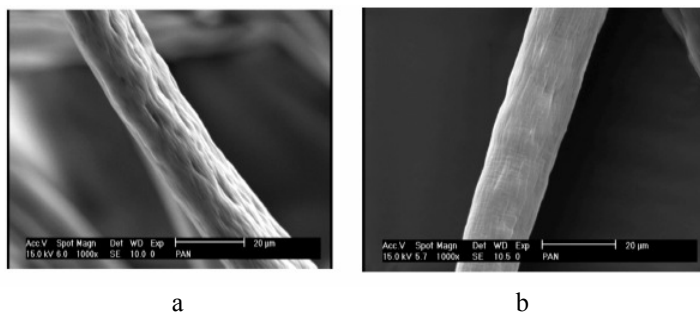


Figure 2. SEM image of (a) the raw fiber and (b) modified PAN fiber

Scanning electron microscopy (SEM) was so used to examine the morphology of the nano fiber before and after modification. As can be seen from Figure 3, original acrylic nano fiber comparatively morphology (Figure 3(a)) and with modified nano fiber (PAN-MMA), obvious change compared to that of the raw fiber was observed (Figure 3 (b)). T 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 iber structure.

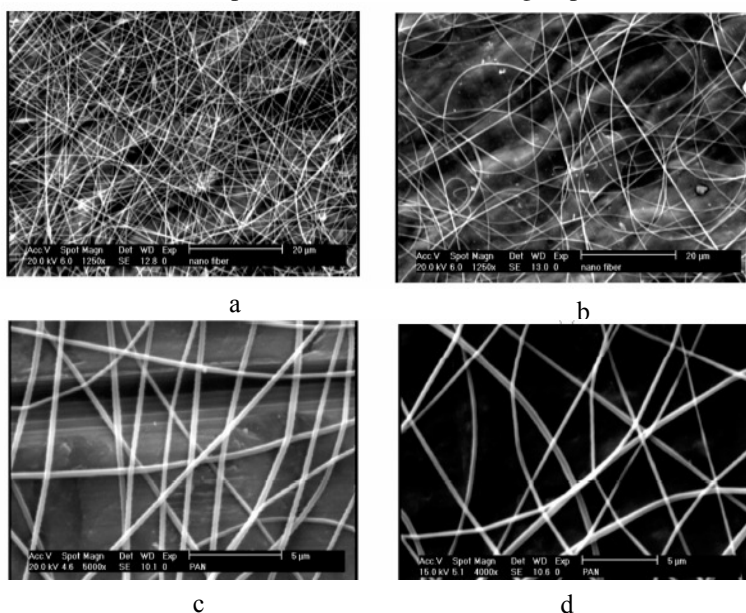


Figure 3. SEM image of (a)(c) the raw nano fiber and (b)(d) modified PAN nano fiber

Selective preconcentration of Cr(III) from natural water for off-line FAAS

This study was undertaken in order to evaluate the potential application of modified nano polyacrylonitrile fiber phase for pre-concentration of trace levels of Cr(III) 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 Cr(III). 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^9 as well as ethylenediaminetetraacetic acid²⁵. However, some of these reagents are usually characterized by adsorption on the surface of modified nano polyacrylonitrile fiber which lead 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 Cr(III), by 10.0 M 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 10.0 M HCl was used for the elution of the adsorbed Cr(III) from the column bed. The pre-concentration factor targeted from this study is 100 as given in Table 4. As the results indicate, the off-line detection results of the eluted and pre-concentrated Cr(III) 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 selective extraction, removal and pre-concentration of Cr(III) by modified nano polyacrylonitrile fiber phase

Table 4. Preconcentration of Cr(III) from DDW and natural tap water samples^a

| Phase, mg | Sample Volume, mL | Cr(III)spiked pg mL^{-1} | Preconcentration reagent | Preconcentration factor | Cr(III)detected ^a ng mL^{-1} | Percentage removal |
|-----------|------------------------|-----------------------------------|--------------------------|-------------------------|--|--------------------|
| 1000 | 2000 Tap water (Saveh) | 20 | 10.0ml of 10.0M HCl | 200 | 3.96 \pm 2.9 | 99.8 \pm 1.9 |
| 1000 | 2000 DDW | 20 | 10.0ml of 10.0 M HCl | 200 | 3.96 \pm 2.9 | 98.7 \pm 1.8 |

^a Values are corrected for blank concentration of water samples and based on triplicate analysis

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