

Solid Phase Extraction of Cr (III) from Natural Water by Modified Nano Polyacrylonitrile Fiber

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Abstract: Modified nano polyacrylonitrile fiber (PANF) was prepared by adding of acrylic fibers to ethanolamine (MEA) 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 potential applications of Modified nano polyacrylonitrile fiber for selective extraction of Cr (III) to occur from aqueous solution were successfully accomplished as well as pre-concentration of low concentration of Cr (III) (60 pg ml^{-1}) from natural tap water with a pre-concentration factor of 100 for Cr (III) off-line analysis by flame atomic absorption analysis.

Key words: Preconcentration . Cr (III) . modified nano polyacrylonitrile fiber

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 agent. The significant drawbacks of Cr (VI) are breathing disturbances, liver and digestion malfunctions, dermal corrosion and skin allergies. 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, FIA-AAS^{38,39}, spectrophotometric^{12,39}, 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 chromium^{18-19,35} 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 UO_2 ³⁴.

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

EXPERIMENTAL

Reagents and materials: 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, Darmstadt, 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 1.0M 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 ethanolamine (MEA) with different concentration solutions. The reaction mixtures were refluxed at 91°C under stirring for 2h. 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 MEA 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 MEA 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 CH₂CHCN (53) and M_1 is the molecular weight of NH₂ (CH₂)₂OH [31, 32].

Activation of surface Modified nano polyacrylonitrile fiber (PANF) was filtered, washed with toluene, ethanol 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, ethanol 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 melt [3]. PAN is solved in common organic solvent. The solubility of Raw Acrylic Fibers (RAF) in dimethylformamide (DMF) was (17:83 w/w) but it was observed that the solubility of PANF-MEA 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 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 upto 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.

2.4 Adsorption and Removed Processes of Metal Ions The adsorption ions onto PANF-MEA 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 258C temperature. The flasks were agitated on a shaker for 2h. The amount of adsorbed metal was determined by the difference between the initial metal ion concentration and the final one after equilibrium [3]. 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:

$$R = (C_0 - C_t) / C_0 \times 100 \quad (2) \quad q = (C_0 - C_t) / G \times V \quad (3)$$

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-MEA fiber sample (in gram). The metal ions adsorbed on the PANF-MEA were then removed by placing 0.1 g of metal loaded fiber in 10 ml of 1M HNO₃ solution for 30 minutes [28].

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 0.1M Cr (III) and 9.0 ml of 0.1M 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 0.1M metal ion and 9.0 ml of the buffer solution (pH 1-6 and 0.1M 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 0.1M 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 column [27] 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 Flame Atomic Absorption Spectrometric analysis (FAAS).

Pre-concentration 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 0.1M 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 Cr (III), this ion was used to evaluate the stability measurements for the Modified nano polyacrylonitrile fiber phase [14]. 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 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 matrix [9]. 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.

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

pH	Cr (III)	Pb (II)	Hg (II)	Mn (II)	Fe (III)	Co (II)	Ni (II)	Cu (II)	Zn (II)	Cd (II)	Ca	Mg	%D
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	0	5	15	5	6
1	10	3	3	13	6	5	14	14	0	0	2	0	2

^aValues are based on n=3 with standard deviation of 4

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 compiles 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].

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 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 phases (25).

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 rules [17]. Third are the notably high $\mu\text{mol g}^{-1}$ values determined for chemically modified 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 [21] 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

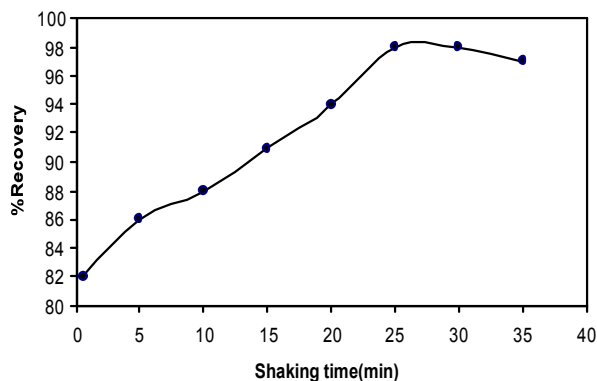


Fig.1: Effect of shaking time (min) on the percentage extraction of Cr (III) by the Modified nano polyacrylonitrile fiber phases

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, 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 (Section 3.1).

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

Metal ions	K_d
Cr (III)	190
Mn (II)	98
Fe (III)	78
Co (II)	70
Ni (II)	60
Cu (II)	760
Zn (II)	445
Cd (II)	115
Cr (III)	12000
Pb (II)	190

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±2
50	500	96±4
100	500	94±5
10	1000	99±4
50	1000	98±3
100	1000	98±5

^aValues are based on triplicate analysis

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 derivatives [9]. 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 systems [10]. The column technique is characterized by major advantages over the batch or static equilibration method that is the possible application to large sample volumes [14-16]. 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 [21]. 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 0.1M 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 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.

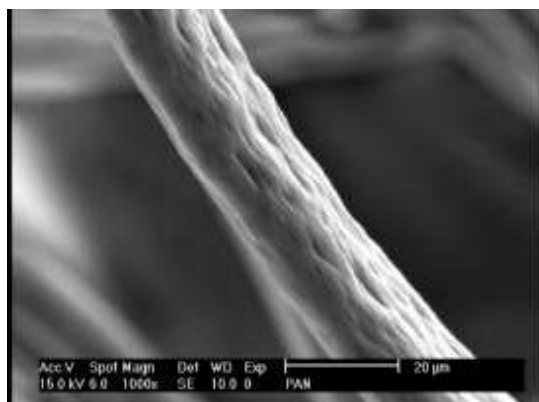
SEM investigations: Scanning electron microscopy (SEM) was used to examine the external surface of the fiber before and after modification. As can be seen from Fig.2, original acrylic fiber comparatively surface (Fig.2a) and with modified fiber (PANF-MEA), obvious change comparing to that of the RAF fiber was observed (Fig.2b). It is clear that changes have occurred in the morphology of the fiber but photographs demonstrated that the surface of PANF-MEA 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.

Scanning electron microscopy (SEM) was so used to examine the morphology of the nano fiber before and after modification. As can be seen from Fig.3, original acrylic nano fiber comparatively morphology (Fig.3a) and with modified nano fiber (PAN-MEA), obvious change compared to that of the raw fiber was observed (Fig.3b). The modified nano fiber was rounder as that of raw acrylic nano fiber. This can be related to modification treatment and incorporation of new functional groups into the fiber structure.

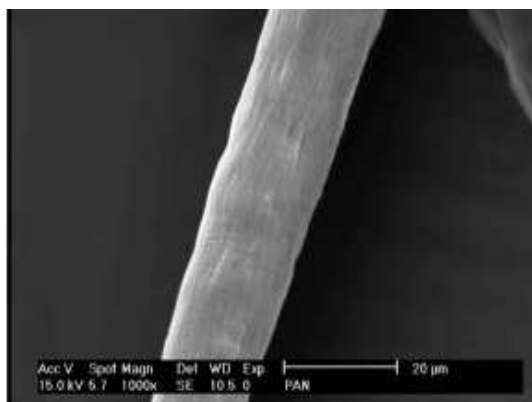
Table 4: Preconcentration of Cr (III) from DDW and natural tap water samples^a

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 (Savch)	20	10.0 ml of 10.0 M HCl	200	3.96±2.5	99.6±1.6
1000	2000 DDW	20	10.0 ml of 10.0 M HCl	200	3.94±2.4	98.4±1.7

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

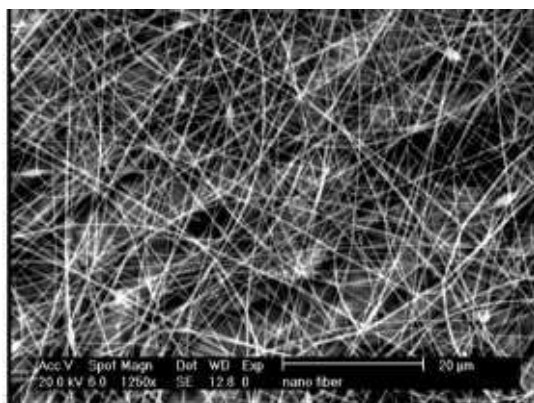


(a)

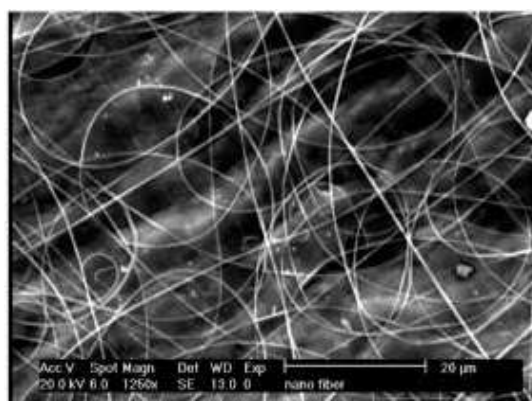


(b)

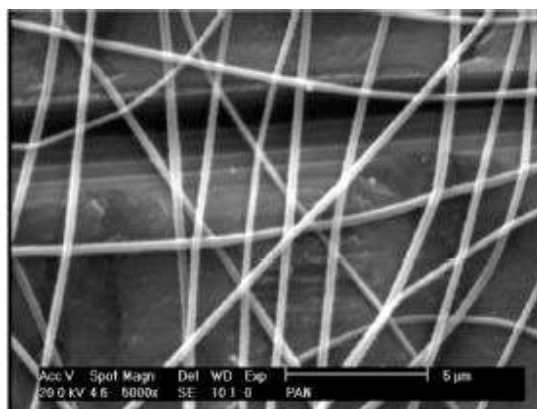
Fig.2: SEM image of (a) the raw fiber and (b) modified PAN fiber



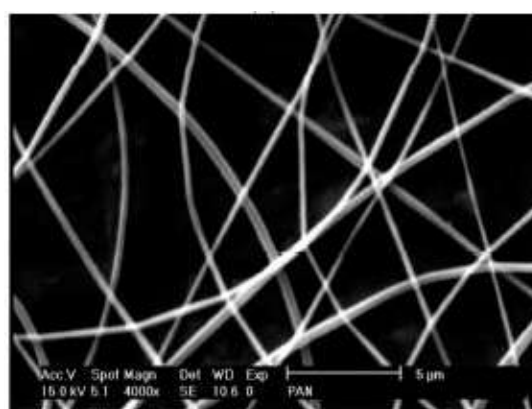
(a)



(b)



(c)



(d)

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

Selective pre-concentration 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 $\mu\text{g ml}^{-1}$ 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 acid [25]. 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 10.0M 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 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

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