

Solid Phase Extraction of Trace Copper(II) Using Modified Nano Polyacrylonitrile Fiber

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Abstract: A simple method has been developed for the preconcentration of copper(II) based on the adsorption of its Modified nano polyacrylonitrile fiber. Modified nano polyacrylonitrile fiber (PANF) was prepared by adding of acrylic fibers to methacrylamide (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. Cu (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 Cu (II) to occur by Modified nano polyacrylonitrile fiber. The potential applications of Modified nano polyacrylonitrile fiber for selective extraction of Cu(II) to occur from aqueous solution were successfully accomplished as well as pre-concentration of low concentration of Cu(II) (60 pg ml^{-1}) from natural tap water with a pre-concentration factor of 100 for Cu(II) off-line analysis by flame atomic absorption analysis.

Keywords: Preconcentration; copper(II), Modified nano polyacrylonitrile fiber

INTRODUCTION

Copper at trace concentrations acts as both a micronutrient and a toxicant in marine and fresh water systems [1-8]. This element is needed by plants at only very low levels and is toxic at higher levels. At these levels, copper can bind to the cell membrane and hinder the transport process through the cell wall. Copper at nearly 40 ng mL^{-1} is required for normal metabolism of many living organisms [9, 10]. On the other hand, copper is an important element in many industries. Thus, the development of new methods for selective separation, concentration and determination of it in sub-micro levels in different industrial,

medicinal and environmental samples is of continuing interest. The determination of copper is usually carried out by flame and graphite furnace atomic absorption spectrometry (AAS) [11, 12, 50] as well as spectrometric methods [13, 14]. However, due to the presence of copper in medicinal and environmental samples at low levels, its separation from other elements presents and also the use of a preconcentration step prior to its determination is usually necessary.

Different methods, especially Liquid-Liquid extraction of copper in the presence of various classical [15-19] and macrocyclic [20,21] co-extractant

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ligands have attracted considerable attention. However, the use of classical extraction methods for this purpose is usually time-consuming, labor-intensive and requires large amounts of high purity solvents for extraction. Nevertheless, several other techniques for the preconcentration and separation of copper have been proposed including liquid chromatography[22] supercritical fluid extraction[23], flotation[24], aggregate film formation[25], liquid membrane[26], column adsorption of pyrocatechol violet-copper complexes on activated carbon[27], ion pairing[28], ion pairing[29], preconcentration with yeast[30], and solid phase extraction using C₁₈ cartridges and disks[31-33,46-49].

Solid phase extraction (SPE) or liquid-solid extraction is popular and growing techniques that are used to sample preparation for analysis. It is an attractive alternative for classical liquid-liquid extraction methods that reduce solvent usage and exposure, disposal costs and extraction time for sample separation and concentration purposed [34-36]. In recent years, the octadecyl-bonded silica SPE disks have been utilized for the extraction and separation of different organic compounds from environmental matrices[37-40]. Moreover, the SPE disks modified by suitable ligands are successfully used for selective extraction and concentration of metal ions [41-42]. In a recent series of papers [43-45] we have described the application of metal-DNA conjugates to nucleic acid sequence determination with catalytic signal amplification; the assay relies on the esterase activity of a DNA-linked Cu complex. For optimization of the system and exploration of structure- activity relationships, a sensitive probe would be useful, which allows straightforward detection of esterase activity of ligated Cu²⁺ in low concentration.

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

EXPERIMENT

Reagents and materials

Analytical grade nitrate salts of Hg, Mn, Fe and Cu(II) 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 1.0M 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 methanolamine (MMA) 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 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), and 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 Cu (II) was performed with a Perkin-Elmer 2380 flame atomic absorption spectrometer. Cu (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 [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-MMA 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 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 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:

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

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

Where C₀ 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 gram). 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 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 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 0.1M Cu (II) 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), Co(II), Cr(III), Zn(II), Fe(III), Hg(II), Mg(II), Mn(II), Ni(II), Pb(II) and Cu(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 Cu (II) by the static technique. In this, 100 mg of the Modified nano polyacrylonitrile fiber phase was added to 1.0 ml of 0.1M Cu(II) 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 Cu(II) from aqueous solutions

One liter of Cu (II) 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 Cu (II) from aqueous and natural tap water

Two liters sample solution spiked with 20 pg ml^{-1} of Cu (II) 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 desorbed the bound-Cu(II). 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

Fig 1 shows TEM images of the nano polyacrylonitrile fiber. The fibers are approximately 100 – 200 nanometers in diameter. As the fibers themselves have a small diameter, the thickness of the nanoweb can likewise be quite small. The thin nanoweb has limited mechanical properties that preclude the use of conventional web handling and filter pleating equipment. As a result, nanofiber 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. Substrates are often chosen to resemble a conventional filter material,

which allows the use of conventional filter media pleating and element handling equipment.

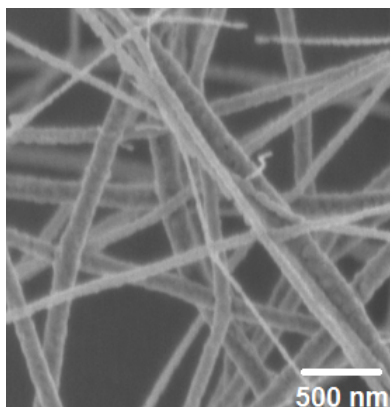


Fig 1. TEM images of the nano polyacrylonitrile fiber

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 Cu (II), 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 Cu (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 [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.

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) Zn(II), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Cd(II), Cr(III) and Pb(II). Several trends can be observed and outlined from the data given. First, it 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, it is the strong affinity of the Modified nano polyacrylonitrile fiber phase for extraction and removal of Cu (II) 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].

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

pH	Cu(II)	Pb(II)	Hg(II)	Mn(II)	Fe(III)	Co(II)	Ni(II)	Zn(II)	Cd(II)	Ca	Mg	Ba
NaOAc	248	59	52	20	-	14	43	63	19	23	20	30
6	217	45	36	58	-	35	64	91	39	21	28	38
5	136	33	23	69	10	50	69	75	20	35	29	29
4	55	25	15	50	44	25	38	60	10	30	15	20
3	34	12	10	28	30	14	38	45	5	25	10	13
2	23	7	8	18	23	10	25	25	00	15	5	6
1	2	3	3	13	3	4	15	14	00	2	00	2

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

This behavior of Modified nano polyacrylonitrile fiber –loaded sulfur containing compounds for selective extraction and removal of Cu(II) from aqueous and natural water sample is well documented [19, 20] and reported based on different governing rules [17]. Third, they 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 active donor atoms (N) directed with the capability and accessibility for fast and direct interactions with the free metal ion present in solution. Fourth, they 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 Cu

(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 $\mu\text{mol g}^{-1}$ and correlated to that determined at 30 min shaking time. Fig. 2 represents the percentage extraction versus shaking time in min and clearly reflects the rapid exchange equilibrium between Modified nano polyacrylonitrile fiber phase and Cu (II). 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).

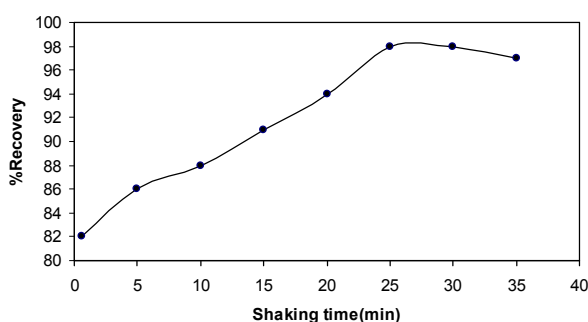


Fig 2. Effect of shaking time (min) on the percentage extraction of Cu(II) by the Modified nano polyacrylonitrile fiber phases.

The distribution coefficient (K_d) data of the tested metal ions with the two newly Modified polyacrylonitrile fiber phase are summarized in Table 2.

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

Metal ions	K_d
Mn(II)	89
Fe(III)	70
Co(II)	76
Ni(II)	65
Zn(II)	800
Cd(II)	499
Cr(III)	500
Cu(II)	12200
Pb(II)	130

It is evident that Cu (II) is the strongest sorted metal ion by Modified nano polyacrylonitrile fiber phase. The distribution coefficient values of Cu (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 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 Cu (II) which behavior can be interpreted on the basis of the affinity of both nitrogen and hidroxil 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 Cu(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 Cu(II) 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 Cu (II) 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 Cu(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 Cu (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 Cu (II). In addition, the effect of packing amount of silica gel phase is also evident in Table 3, where the near completion of Cu (II) removal was accomplished by the use of 1000 mg phase.

Table 3. Percentage removal of Cu (II) from aqueous solutions by Modified nano polyacrylonitrile fiber phase ^a

Cu(II) spiked (ng ml ⁻¹)	Phase (mg)	Percentage removal
10	500	96±2
50	500	98±3
100	500	98±2
10	1000	97±3
50	1000	98±2
100	1000	96±2

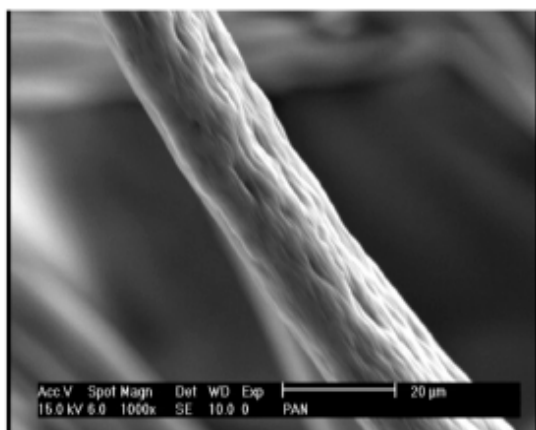
^a Values are based on triplicate analysis.

SEM Investigations

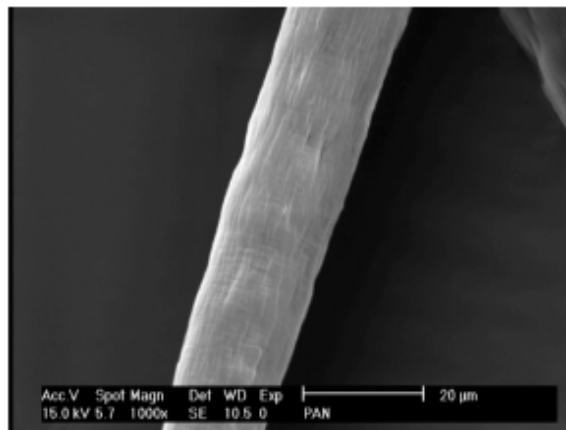
Scanning electron microscopy (SEM) was used to examine the external surface of the fiber before and after modification. As can be seen from Fig. 3, original acrylic fiber comparatively surface (Fig. 3(a)), and with modified fiber (PANF-MMA), obvious change comparing to that of the RAF fiber

was observed (Fig.3(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.

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. 4, original acrylic nano fiber comparatively morphology (Fig. 4(a)), and with modified nano fiber (PAN-MMA), obvious change compared to that of the raw fiber was observed (Fig.4 (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 fiber structure.



(a)



(b)

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

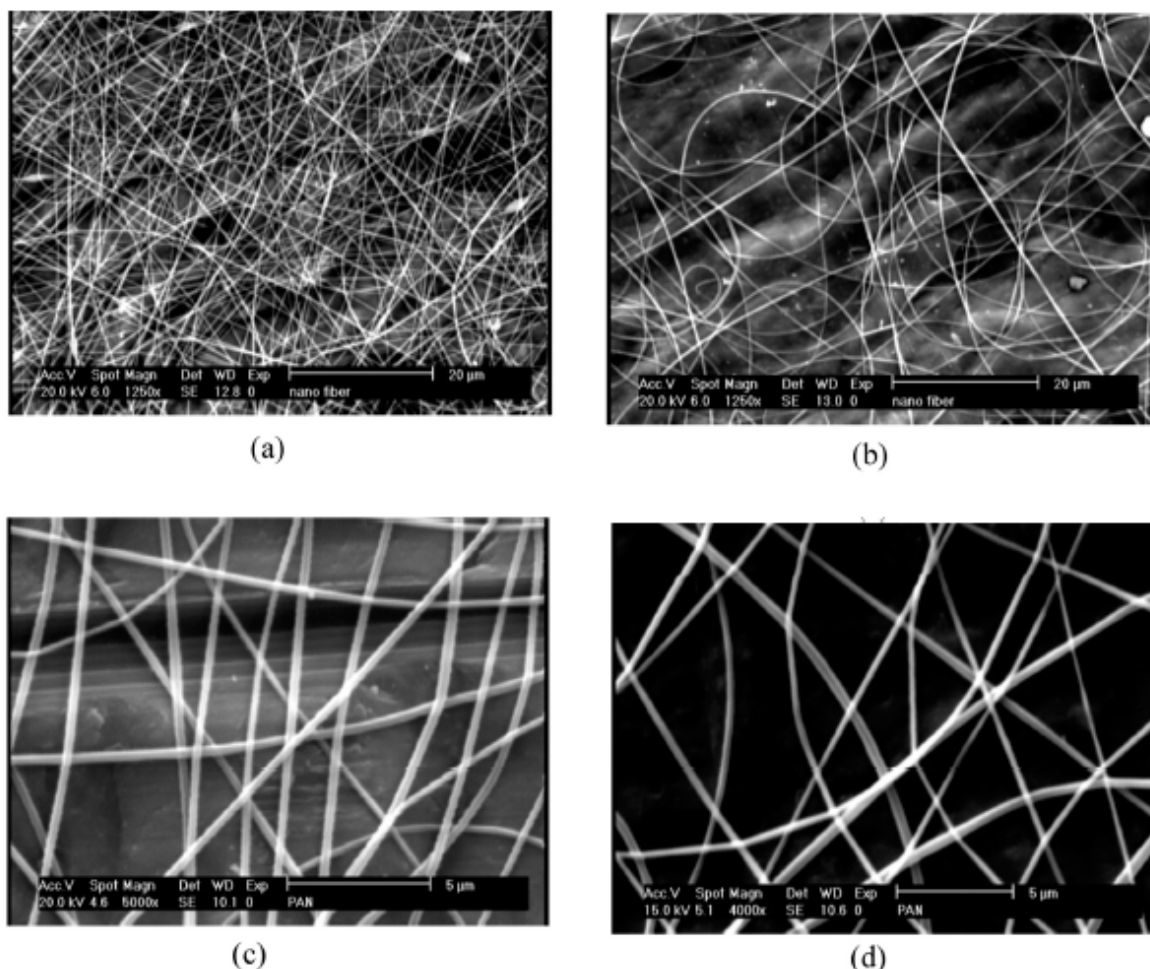


Fig 4. SEM image of (a)(c) the raw nano fiber and (b)(d) modified PAN nano fiber

Selective pre-concentration of Cu(II) 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 Cu (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 $\mu\text{g ml}^{-1}$ of Cu (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 [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 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 Cu(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 Cu (II) from the column

bed. The pre-concentration factor targeted from this study is 100 as given in Table 4.

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

Phase (mg)	Sample Volume(mL)	Cu(II)spiked (pg ml ⁻¹)	Preconcentration reagent	Preconcentration factor	Cu(II)detected ^a (ng ml ⁻¹)	Percentage removal
1000	2000	20	10.0ml of 10.0M HCl	200	3.95±2.6	98.4±1.9
1000	2000	20	10.0ml of 10.0 M HCl	200	3.94±2.7	98.4±1.9

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

As the results indicate the off-line detection results of the eluted and pre-concentrated Cu(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 selective extraction, removal and pre-concentration of Cu (II) by Modified nano polyacrylonitrile fiber phase.

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