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Preconcentration of Zn(II) in Water Sample Using Modified NanoFiber

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ABSTRACT

A new simple and reliable method for rapid and selective extraction and determination of trace levels of Zn(II) ion is developed. Zn(II) ions are adsorbed quantitatively during passage of aqueous samples through PET-AA/AAm nano fiber modified. Almost all matrix elements were found to pass through the nano fiber to drain. Modified Poly (ethylene terephthalate)-grafted-Acrylic acid/Acryl amide Nano fiber was prepared by adding of acrylic nano fibers to methanolamine (PET-AA/AAm) with different concentration solutions. The stability of a chemically modified PET-AA/AAm nano fiber especially in concentrated hydrochloric acid which was then used as a recycling and pre-concentration reagent for further uses of Modified PET-AA/AAm nano fiber. The application of this modified PET-AA/AAm nano 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. Zn(II) was found to exhibit the highest affinity towards extraction by these modified PET-AA/AAm nano 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 Zn(II) to occur by modified PET-AA/AAm nano fiber. The potential applications of modified PET-AA/AAm nano fiber for selective extraction of Zn(II) to occur from aqueous solution were successfully accomplished as well as pre-concentration of low concentration of Zn(II) (60 pg ml^{-1}) from natural tap water with a pre-concentration factor of 100 for Zn(II) off-line analysis by flame atomic absorption analysis.

Keyword: Preconcentration; Zn(II); Modified Poly (ethylene terephthalate)-grafted-Acrylic acid/Acryl amide Nano fiber(PET-AA/AAm).

1. INTRODUCTION

Zinc is considered as an essential micronutrient for humans, plants and animals. It plays an important role in several biochemical processes [1]. Zinc deficiency slows growth and development of the

neonate. Zinc deficiency also leads to cognitive defects and impairs the immune system [2]. However, if it is in excess, it can also play an important role in the progression of several damages to human body, including disturbances in energy metabolism or increasing in oxidative stress [3]. Therefore, it is of great importance and significance for environment science and life science to separate and determine trace zinc in water samples. Although very sensitive analytical techniques, such as FAAS [4,5,19-20], ICP-MS [6] and ICP-AES [7] are used for the determination of trace zinc. In order to achieve accurate and reliable results, preconcentration step is necessary when the concentration of zinc is too low to be directly determined. Solid-phase extraction (SPE) is one of the most effective preconcentration methods because of simplicity, rapidity, high preconcentration factor and high recovery. The procedures for separation and preconcentration of zinc had been reported extensively [4-13]. Polyurethane foam loaded with 2-[2-(6-methyl-benzothiazolylazo)]-4-bromophenol [8] was used for separation of zinc in natural water samples. Silica gel functionalized with 1,5-bis(di-2-pyridyl)methylene thiocarbohydrazide [7], 1,8-dihydroxyanthraquinone [9] were used for the preconcentration of zinc in water samples. Ion flotation [10], Amberlite XAD-2 [11,12], solvent extraction using LIX 84 I [13], poly(ethylene terephthalate), naphthalene [17,18] were also used for the separation of zinc in diverse samples.

However, using microcrystalline triphenylmethane loaded with malachite green as solid-phase extractant to separate and preconcentrate Zn(II) has not been reported in any literature. Some analogous compounds of BTMQ such as 2-(6-methyl-2-benzothiazolylazo)-5-diethyl aminophenol (MBTAE) [22-24] and 2-(2-thiazolylazo)-5-diethylaminophenol (TADAP) [25-27] have been applied as a precolumn derivatizing reagent in high-performance liquid chromatography (HPLC). Another analogue, 2-(6-bromo-2-benzothiazolylazo)-5-diethyl aminophenol, was synthesized and applied to the spectrophotometric determination of nickel [28] and zirconium [29].

This paper describes the applications of Modified Poly (ethylene terephthalate)-grafted-Acrylic acid/Acryl amide Nano fiber(PET-AA/AAm) for selective extraction and solid phase pre-concentration of Zn (II) from aqueous and natural water samples.

2. EXPERIMENTAL

2.1. Reagents
Nano fiber PET (filaments: 130 and dtex 170) made in Textile Engineering Department, Amir Kabir University of technology, Tehran, Iran. Analytical grade nitrate salts of Acrylic acid, acryl amid, benzoyl peroxide, acetone, Hg, Mn, Fe and Zn(II), Li, Na, K, Mg, Ca, Sr, Ba, Zn, Cd, Pb(II), Ni(II), Co(II) and Cu(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 1.0M HCl; HNO_3 were mixed and the pH-value of the resulting solution was adjusted with the use of a pH-meter.

2.1.1. Preparation of Modified PET-AA/AAm nano fiber
Nano fiber samples (0.100 / 0.001 g) were placed in a 100 mL polymerization tube and calculated amount of AA and AAm were added to it. Then Bz_2O_2 dissolved in 3 mL acetone was added to tube. The mixture was made up to 50 mL with deionized water and placed into a water bath at the polymerization temperature 85-61°C for 2 h. The nano fiber samples taken at the end of polymerization were freed from homopolymer or copolymers by washing with boiling water and acetone for 1 h (changing the washing water four times). The washed nano fiber was dried at 50°C under vacuum. The methodology used
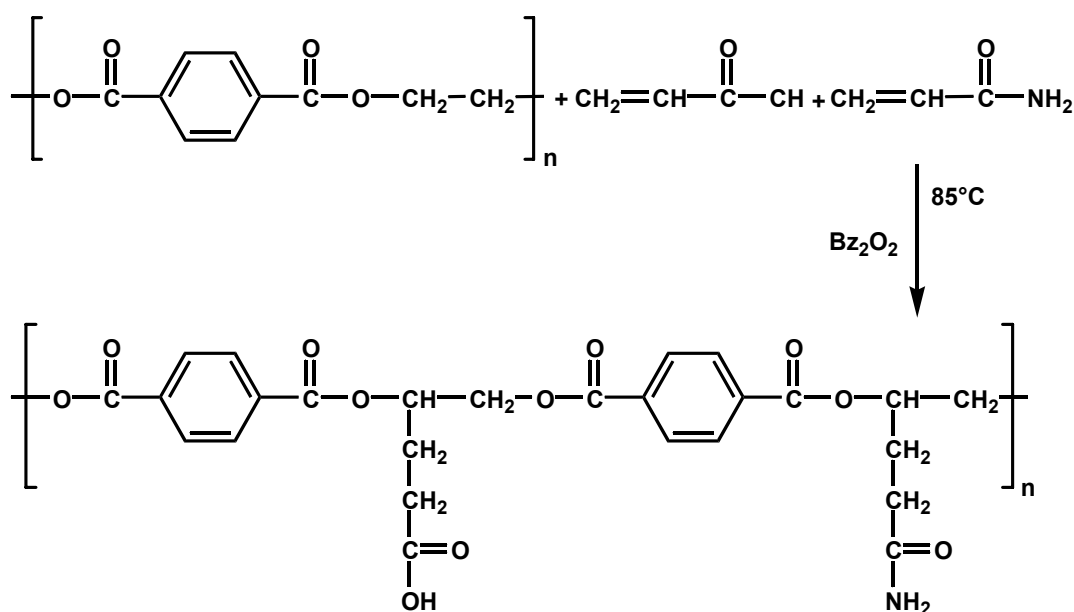
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Figure 1: *Schematic representation of the methods of polymer modification [24].*

to synthesize modified PET is summarized in Figure 1.

The content of the PET-AA/AAm groups in the nano fiber was calculated as follows:

$$E_A = \frac{(W_1 - W_0)M_0}{(M_1 W_0)} \tag{1}$$

where E_A is the content of PET-AA/AAm groups in the nano fiber(mol/g), W_1 is the weight of the dry nano fiber after reaction (g), W_0 is the weight of the dry nano fiber before reaction (g), M_0 is the molecular weight chain unit $CH_2CHCN(53)$, AND M_1 is the molecular weight of $NH_2(CH_2)_2OH$ [31,32]. Activation of surface Modified PET-AA/AAm nano fiber 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 PET-AA/AAm nano fiber. 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.

2.2. 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 PET-AA/AAm nano fiber were carried out from KBr pellet by a Perkin-Elmer 1430 ratio recording spectrophotometer. Atomic absorption analysis of all the metal ions except Zn(II) were performed with a Perkin-Elmer 2380 flame atomic absorption spectrometer. Zn(II) determinations were performed by a Varian Spect AA-10. Raman spectrophotometer analysis were performed with a Perkin-Elmer.

2.3. Electro Spinning
The formation of a thin nano fiber via electrospinning is based on the uniaxial stretching (or elongation) of a viscoelastic jet derived from a polymer solution or melt [3]. PET-AA/AAm is solved in common organic solvent. The solubility of Poly (ethylene terephthalate) nano fibers in dimethylformamide (DMF) was (17:83 w/w) but it was observed that the solubility of PET-AA/AAm 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 m^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 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.

Adsorption and Removed Processes of Metal Ions The adsorption ions onto PET-AA/AAm 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 258°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 [3]. The concentration of ions was determined with a flame atomic absorption (FAA) spectrometer (PG990).

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

$$R = \frac{(C0 - Ct)}{C0} \times 100$$

$$q = \frac{(C0 - Ct)}{G \times V}$$

where C0 is the initial metal ion concentration (mg/l), Ct is the ion concentration after the adsorption period, V is the volume of solution L and G is the dry mass of the PET-AA/AAm nano fiber sample (in gram). The metal ions adsorbed on the PET-AA/AAm were then removed by placing 0.1 g of metal loaded nano fiber in 10 ml of 1M HNO_3 solution for 30 minutes [28].

2.4. Stability studies

The stability of modified PET-AA/AAm nano 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 Zn(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 Poly (ethylene terephthalate) from the surface of modified PET-AA/AAm nano fiber phases in different acidic solutions was calculated from the determined $\mu mol \ g^{-1}$ value of each treated phase.

2.5. Sorption studies

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

The determination of metal capacity of 13 metal ions, viz. Ba(II) Ca(II), Co(II), Zn(II), 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 Zn(II) by the static technique. In this, 100 mg of the modified PET-AA/AAm nano fiber phase was added to 1.0 ml of 0.1M Zn(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.

2.5.2. Determination of the distribution coefficient

About 100 mg of the modified PET-AA/AAm nano fiber phase was mixed with 50 ml of the metal ion (1 mgml^{-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.

2.5.3. Percentage removal of Zn(II) from aqueous solutions

One liter of Zn(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 PET-AA/AAm nano 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).

2.5.4. Pre-concentration of Zn(II) from aqueous and natural tap water

Two liters sample solution spiked with 20 pg ml^{-1} of Zn(II) in both double destilled water (DDW) and natural tap water were prepared and passed over a column packed with 1000 mg of modified PET-AA/AAm nano fiber with a flow rate of 2ml 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-Zn(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.

3. RESULTS AND DISCUSSION

Figure 2 shows TEM images of the PET-AA/AAm nano fiber. The nano fibers are approximately 100-200 nanometers in diameter. As the nano 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, 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. Substrates are often chosen to resemble conventional filter materials, which allows the use of conventional filter media pleating and element handling equipment.
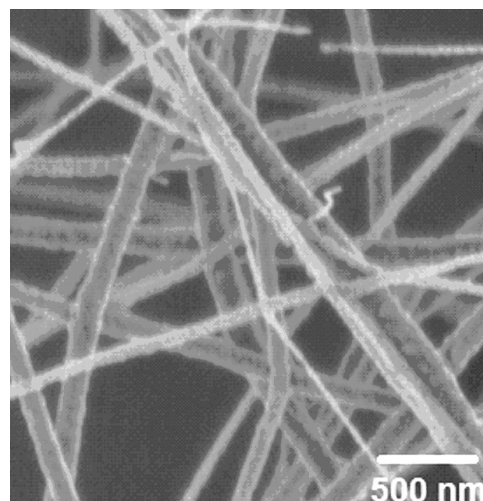

Figure 2: *TEM images of the PET-AA/AAm nano fiber.*

3.1. Stability studies

The stability of the newly synthesized modified PET-AA/AAm nano 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 Zn(II), this ion was used to evaluate the stability measurements for the modified PET-AA/AAm nano fiber phase [14]. The results of this study proved that the modified PET-AA/AAm/AAm nano 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, 10.0 M) was found to change the color of modified PET-AA/AAm nano fiber from dark brown into reddish brown which is interpreted on the basis of chemical changes of the organic PET-AA 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 PET-AA/AAm/AAm nano fiber phase compared to non-treated silica gel phases judging from the color change of the two phases as well as

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the metal capacity values determination of Zn(II) and comparison of these with those of the original non-treated modified PET-AA/AAm/AAm nano 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 PET-AA/AAm/AAm nano fiber phases were also found to be stable over a range of 1 year during the course of this work.

3.2. Metal capacity in various controlling factors

The metal capacity values determined in $\mu mol\ g^{-1}$ for the modified PET-AA/AAm/AAm nano fiber in different buffer solutions were studied to evaluate the pH effect of metal ion on the extractability of the modified PET-AA/AAm/AAm nano fiber phase. Table 1 compiles the $\mu mol\ g^{-1}$ 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, is the strong dependence of $\mu mol\ g^{-1}$ 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 PET-AA/AAm/AAm nano fiber phase for extraction and

removal of Zn(II) from aqueous solution compared to other tested metal ions, as shown by the higher $\mu mol\ g^{-1}$ values by modified PET-AA/AAm/AAm nano fiber phases (25).

This behavior of modified PET-AA/AAm/AAm nano fiber-loaded sulfur containing compounds for selective extraction and removal of Zn(II) from aqueous and natural water sample is well documented [19,20] and reported based on different governing rules [17]. Third are the notably high $\mu mol\ g^{-1}$ values determined for chemically modified PET-AA/AAm/AAm nano fiber phase in comparison with values found as given in Table 1. The comparison between the metal sorption properties of chemically and physically-modified PET-AA/AAm/AAm nano 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 PET-AA/AAm/AAm nano 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

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

pH	Zn(II)	Pb(II)	Hg(II)	Mn(II)	Fe(III)	Co(II)	Ni(II)	Cu(II)	Cd(II)	Ca	Mg	Ba
NaOAc	248	59	52	20	-	14	43	63	19	23	20	20
6	217	45	36	58	-	35	64	91	39	21	23	28
5	136	33	23	69	10	50	69	74	20	35	2l	29
4	55	25	15	50	44	25	38	60	10	30	19	10
3	34	12	10	28	30	14	38	45	5	25	10	10
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.
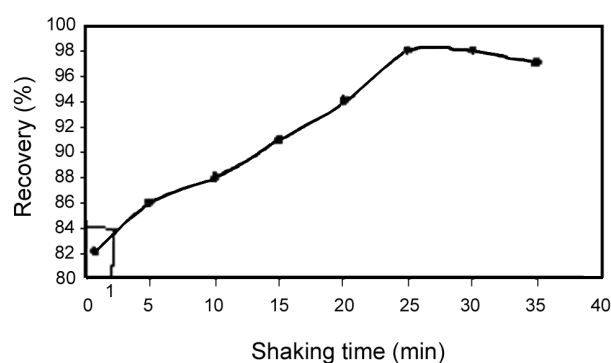
Figure 3: *Effect of shaking time (min) on the percentage extraction of Zn(II) by the modified PET-AA/AAm/AAm nano fiber phases.*

similar. Therefore, the conclusion drawn from this section can be outlined as the high superiority of phase for selective extraction of Zn(II) as well as the higher metal uptake behavior of modified PET-AA/AAm/AAm 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 3 represents the percentage extraction versus shaking time in min and clearly reflects the rapid exchange equilibrium between modified PET-AA/AAm /AAm nano fiber phase and Zn(II). One minute shaking time was found to be sufficient to establish 84% of the determined μmol g^{-1} value at 30 min

Table 2: *Distribution coefficient (Kd) values of various metal ions.*

Metal ions	K_d
Mn(II)	59
Fe(III)	47
Co(II)	78
Ni(II)	65
Cu(II)	800
Cd(II)	590
Cu(II)	318
Zn(II)	1250
Pb(II)	730

whereas 10 min shaking time led to 88% extraction. The data and results presented in this section reveal the superiority of modified PET-AA/AAm/AAm nano fiber phase as previously declared in the stability studies (Section 3.1).

The distribution coefficient (K_d) data of the tested metal ions with the two newly Modified polyacrylonitrile nano fiber phase are summarized in Table 2. It is evident that Zn(II) is the strongest sorbed metal ion by modified PET-AA/AAm/AAm nano fiber phase. The distribution coefficient values of Zn(II) by the loaded modified PET-AA/AAm /AAm nano fiber phase were found to be much higher than those reported for ion exchange resins containing modified PET-AA/AAm/AAm nano fiber derivatives [9]. In addition, the K_d values for Zn(II) by modified PET-AA/AAm/AAm nano fiber phase were found to come on the second place after Zn(II) which behavior can be interpreted on the basis of the affinity of both nitrogen and hidroxyl donor groups present in modified PET-AA/AAm /AAm nano fiber for binding with Zn(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 PET-AA/AAm /AAm nano fiber phase judging from the comparable low distribution coefficient values determined for these metal ions. The higher K_d value for Zn(II) and the lower ones for the other metal ions, except Zn(II), provide an additional evidence for the suitability of these two newly modified PET-AA/AAm/AAm nano fiber phase for selective extraction of Zn(II) from aqueous solutions. It is also noteworthy that the conclusion drawn from the evaluation of the K_d values by modified PET-AA/AAm/AAm nano fiber phase is consistent with the reported data.
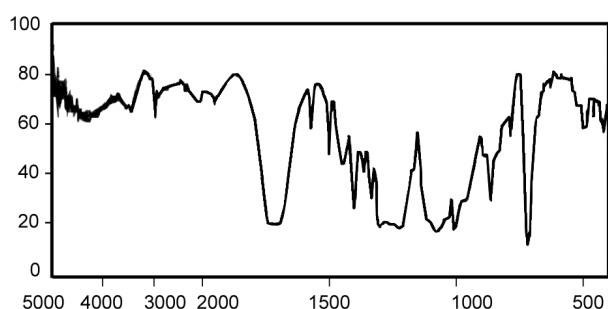
3.3. IR Spectrum
The IR spectrum of PET-AA/AAm is compared with free PET (Figure 4). There are two additional bands at 2096-3078 and 1787 cm^{-1} which appear to originate due to NH_2 and amidic C=O.

3.4. Raman spectroscopy
Raman spectrum of PET-AA/AAm (cm^{-1}): 1612

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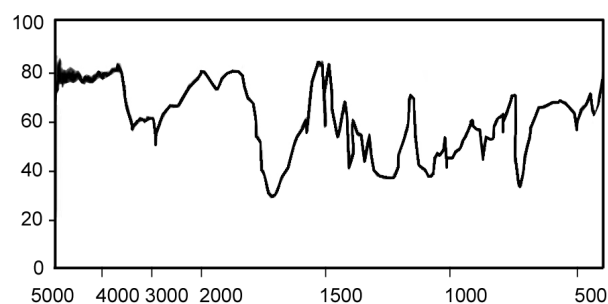
(a)

(b)

Figure 4: *FT-IR spectrum of PET (a) and PET-AA/ AAm (b) [24].*

aromatic (C=C), 1728(amidic C=O), 1058 and 1117 (C-O), 3000 aromatic (C-H) and both 2996 and 3100 (NH$_2$). Raman spectrum of PET-AA/AAm loaded Zn (II) (cm^{-1}): 1611 aromatic (C=C), 1732 (amidic C=O), 1085, 1125 (C-O), 3003 aromatic (C-H) and both 2965 and 3100 (NH$_2$).

The band observed in the PET-AA/AAm at 2996, 1728, 1117 cm^{-1} can be assigned to (NH$_2$) stretching vibration, (C=O) and (C-O) shift to 2965, 1732, and 1127 cm^{-1} in PET-AA/AAm- Zn^{2+}, respectively. These results demonstrate the amidic and acidic groups on the grafted polymer interact with Zn^{2+} and confirm the formation of PET-AA/AAm- Zn^{2+} complex.
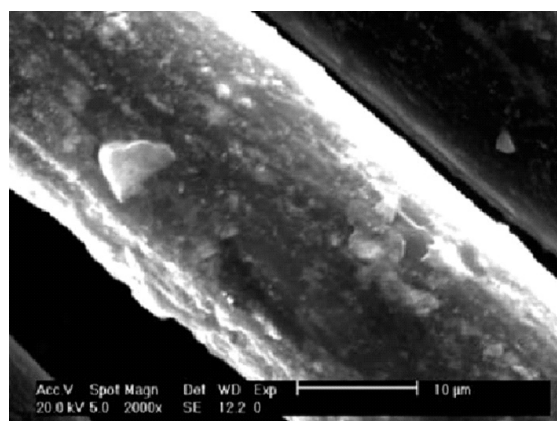
3.5. Scanning electron microscopy

SEM was used to examine the external surface of the nano fiber after modification and metal ions adsorption. The SEM images are presented in Figure 5. The surface of ungrafted PET has a smooth and highly homogeneous appearance. As shown in Figure 5(a,b), in comparison with the
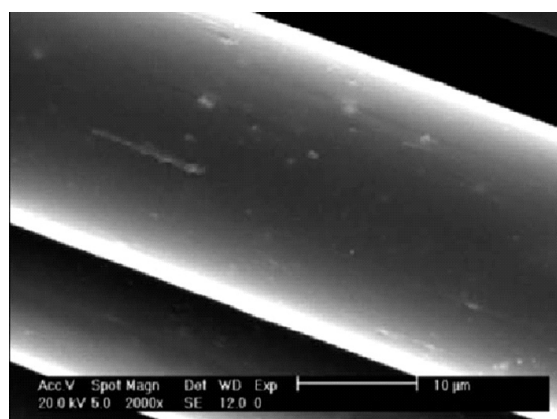
(a)
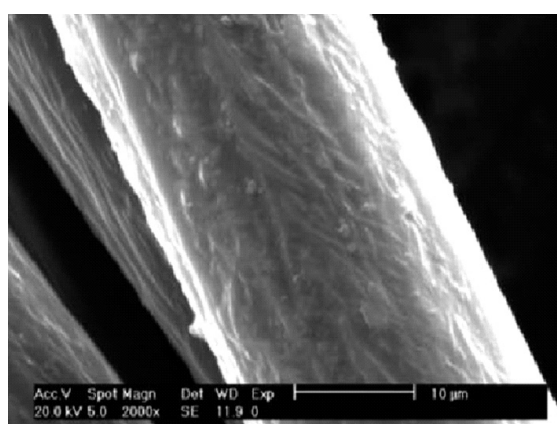
(b)

(c)

Figure 5: *SEM photograph of PET (a), PET-AA/AAm (b) and PET-AA/AAm loaded with metal ion [24].*

surface of the grafted PET, surface of raw PET were less coarse and groovy because PET-AA/AAm nano fiber have grafted chains containing AA and AAM. As seen in Figure 5(c), surface debris on the

nano fibers after metal cation impregnation were observed. This image shows that ion adsorption increases the surface roughness. There is also an increase in diameter of the modified nano fibers. This can be related to the swelling phenomenon.

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 6, original PET-AA/AAm nano fiber comparatively morphology (Figure 6(a)), and with modified nano fiber PET-AA/AAm obvious change compared to that of the raw fiber was observed (Figure 6 (b)). 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.

### 3.6. The effect of the monomer mixture ratios on grafting percentage

To investigate the effect of monomer mixture ratios on the grafting, the graft copolymerization was carried out at different W/V percentage ratios of AA/AAm co monomers by using Bz_2O_2. The experimental results are shown in Figure 7. As seen from Figure 7, when AA was grafted alone on PET nano fibers the maximum grafting percentage was found to be as low as 6.94%. This suggests that AA is not sufficiently reactive toward PET macro radicals. Thus, the amount of AA in PET structure is lower. The use of AAm co monomer in grafting
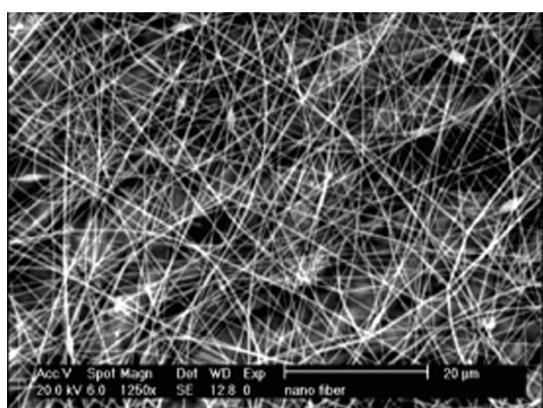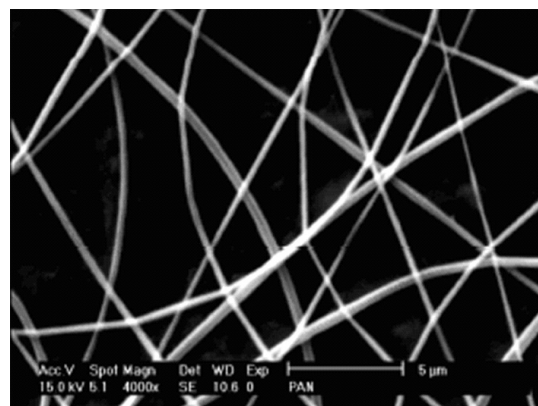

(a)
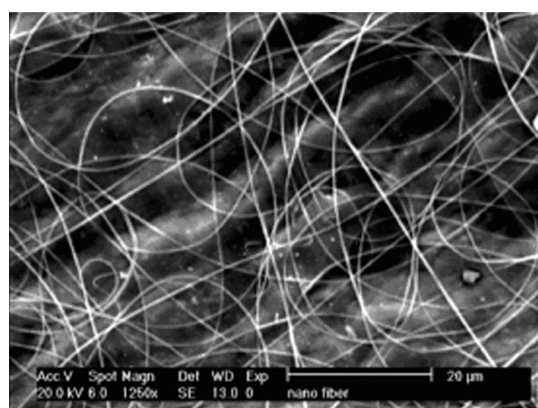
(b)
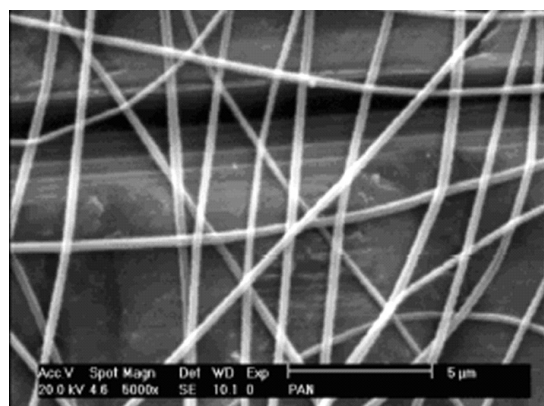
(c)

(d)

Figure 6: SEM image of (a)(c) the raw nano fiber and (b)(d) modified PET-AA/AAm nano fiber.
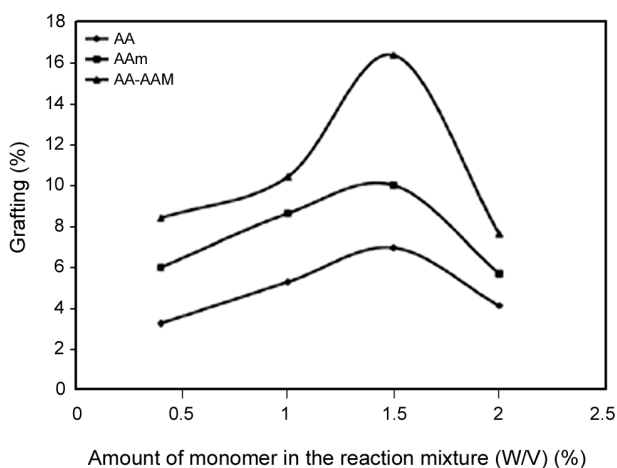
Figure 7: *Effect monomer concentration on grafting percentage [24].*

caused an increase in grafting percentage (9.98%). The grafting percentage was highly dependent on the monomer mixture ratio, and the maximum grafting percentage (16.34%) was reached at an AA/AAm ratio of 30:70. On the nano fibers grafted with the AA/AAm mixture, the side chains contained structural units coming from both AAm and AA.

3.7. Effect of pH

According to the recommended procedure solutions (the volume of each 100 mL) containing 0.5 l g mL^{-1} of Zn(II)was taken. Their pH values
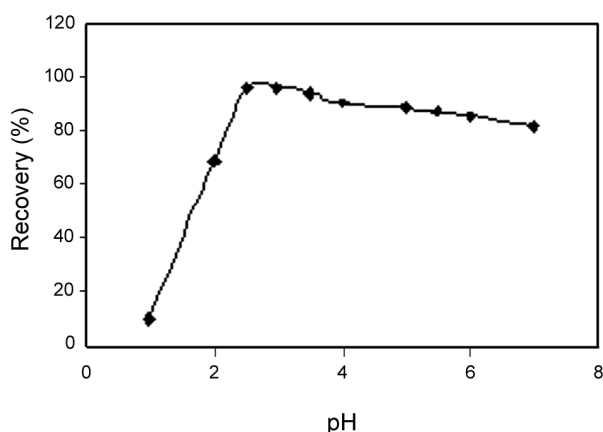

Figure 8: *Effect of pH sorption of Zn(II)onto modified PET-AA/AAm. shaking time: 5 h, temperature: 25°C.*

were adjusted in range 1.5-7 with HNO$_3$, 0.01 M acetate and/or phosphate buffer solutions and the mixture was shaken for 5 h. The 0.1 g of modified PET-AA/AAm nano fiber in different pH value, namely pH 1.5, 2, 3, 4, 5, 6 and 7 Zn(II) was determined. It also can be seen in Figure 8, the sorption quantity of Zn(II) increases with the pH value increases in the studied pH ranges. Below pH 2.0, the sorption quantity of Zn(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.

3.8. Selective pre-concentration of Zn(II) from natural water for off-line FAAS

This study was undertaken in order to evaluate the potential application of modified PET-AA/AAm nano fiber phase for pre-concentration of trace levels of Zn(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 (2l) were spiked with 20 pg ml^{-1} of Zn(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 ethylenediaminete-traacetic acid [25]. However, some of these reagents are usually characterized by adsorption on the surface of modified PET-AA/AAm nano 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 Zn(II), by 10.0 M HCl acid is found to be high without causing any notable change to the chemical nature of the organic modified PET-AA/AAm nano fiber. Therefore, 10.0 ml of 10.0M HCl was used for the elution of the adsorbed Zn(II) from the column bed. The pre-concentration factor targeted from this study is 100 as given. As the results indicate, the off-line detection results of the eluted and pre-concentrated Zn(II) are very good with a satisfactory pre-concentration factor which can be

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further increased to 100-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 Zn(II) by modified PET-AA/AAm nano fiber phase.

3.9. Percentage removal of Zn(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 character-ized 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 Zn(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 PET-AA/AAm /AAm nano fiber phase packing. The results of the percentage removal of Zn(II) from aqueous solutions are presented in Table 3 which clearly

Table 3: Percentage removal of Zn(II) from aqueous solutions by modified PET-AA/AAm/AAm nano fiber phase. [a]

Zn(II) spiked (ng ml^{-1})	Phase (mg)	Percentage removal
10	500	94±2
50	500	96±3
100	500	97±3
10	1000	99±1
50	1000	95±3
100	1000	96±4

[a] *Values are based on triplicate analysis.*

demonstrate the suitability and validity of modified PET-AA/AAm/AAm nano fiber phase for removal and extraction of Zn(II). In addition, the effect of packing amount of silica gel phase is also evident in Table 3, where the near completion of Zn(II) removal was accomplished by the use of 1000 mg phase.

4. CONCLUSIONS

Thus, a selective and sensitive method for the determination of trace levels of Zn(II) based on modified PET-AA/AAm nano fiber as a sorbent for the determination of the analytes in biological samples as well as natural water samples. The sorption capacity for Zn(II) is 44.01 mg g^{-1} that is higher than most of the sorbents. The faster sorption and desorption are other distinct advantages. In comparison to the commonly immobilized in silica gel, the present sorbent has a superior preconcentra-

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

Phase (mg)	Sample Volume(mL)	Zn(II)spiked (pg.ml^{-1})	Preconcentration reagent	Preconcentration factor	Zn(II)detected [a] (ng.ml^{-1})	Percentage removal
1000	2000 Tap water (Saveh)	20	10.0 ml of 10.0 M HCl	200	3.95±2.5	99.4±1.5
1000	2000 DDW	20	10.0 ml of 10.0 M HCl	200	3.93±2.3	98.2±1.7

tion factor (100-folds) for Zn(II). In addition, the preparation of modified PET-AA/AAm nano fiber is relatively simple and rapid. But the modified PET-AA/AAm nano 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.

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