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Preconcentration of Mo(II) on Micro Crystalline Modified with Functionalized-Nano Graphene

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ABSTRACT

A organic-solution-processable functionalized-graphene (SPFGraphene) material has been studied on pre-concentration and determination of trace Mo(II) ions. In this process, the effects of pH solution, elution conditions on pre-concentration of trace Mo(II) were studied and the effect of interfering ions was also investigated. A selective method for the fast determination of trace amounts of Mo(II) ions in water samples has been developed. Method has been developed for preconcentration of Mo on organic-solution-processable functionalized-graphene (SPFGraphene) adsorbent in the pH range 5.0-10.0, prior to its spectrophotometric determination, based on the oxidation of bromopyrogallol red at λ = 517 nm. This method makes it possible to quantitize Mo in the range of 6.9×10^{-9} to 2.7×10^{-5} M, with a detection limit (S/N = 3) of 1.78×10^{-9} M. This procedure has been successfully applied to determine the ultra-trace levels of Mo in the environmental samples, free from the interference of some diverse ions. The precision, expressed as relative standard deviation of three measurements is better than 3.0%.

Keyword: Preconcentration; Micro crystalline; Nano graphene; Mo(II); SPE; FAAS; Organic-solution; Functionalized.

1. INTRODUCTION

Toxicological studies have proved that the degree of toxicity of an element directly depends on the species in which it is present. Mo(II) is a potentially carcinogenic agent [1]. Mo(II) at trace concentrations acts as both a micronutrient and a toxicant in marine and fresh water systems [2-5]. This element is needed by plants at only very low levels and is toxic at higher levels.

At these levels, Mo(II) can bind to the cell membrane and hinder the transport process through the cell wall. Mo(II) at nearly 40 ng mL^{-1} is required for normal metabolism of many living organisms [6]. On the other hand, Mo(II) is an important element in many industries. Thus, the development of new methods for selective separation, concentration and determination of it in

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Int. J. Bio-Inorg. Hybd. Nanomat., Vol. 2, No. 4 (2013), 495-502

Moghimi A

sub-micro levels in different industrial, medicinal and environmental samples is of continuing interest.

The determination of Mo(II) is usually carried out by flame and graphite furnace atomic absorption spectrometry (AAS) [7] as well as spectrometric methods [8].

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. Solid phase extraction determinations can be carried out in different efficient ways. One of the most appropriative preformation features of SPE is achieved by using octadecyl silica membrane disks. SPE reduce the use of toxic solvent, disposal costs, and extraction time [9-11].

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 bed [13].

In our previous attempts, we modified SPE membrane disks with suitable compounds for selective determination of chromium [14] and lead [11]. Meanwhile, other investigators have successfully utilized these sorbents for quantitative extraction and monitoring trace amounts of lead [15], copper [16], silver [19], mercury [17, 19], cadmium [20], palladium [21], Ce [22] and UO_2 [12].

The used ligand is new and fairly selective and will not interfere in the determination process of Mo(II). Absorption spectrophotometry method (after preconcentration) was applied for determination of Mo based on the oxidation of bromopyrogallol red at 517 nm. Various effective parameters have been evaluated, and the developed procedure has been successfully employed for the quantitation of ultra-trace amounts of Mo in water sample.

2. EXPERIMENTAL

2.1. Apparatus
The glass column with 10 mm i.d. and 200 mm height was used to make preconcentration column. An

UV–Vis spectrophotometer WPA Cambridge UK (Diode Array, Model S2000) was applied for recording the absorption spectra. A spectrophotometer (Perkin-Elmer model 35) with 10 mm glass cuvette was used to measure the absorbance at a fixed wavelength. Controlling the reaction temperature was done by a water bath thermostat (Gallenkamp Griffin, BJ-240-V) and a stopwatch was used for recording the reaction time. The synthesis of the TPP-NHCO-SPFGraphene is illustrated in Scheme 1.

2.2. Reagents
Doubly distilled water and analytical-reagent grade chemicals were used throughout.

2.2.1. Synthesis of TPP-NHCO-SPFGraphene
The first organic-solution-processable functionalized-graphene (SPFGraphene) hybrid material with porphyrins was prepared. The synthesis of the porphyrin-Graphene nanohybrid, 5-4 (aminophenyl)-10, 15, 20-triphenyl porphyrin (TPP) and grapheme oxide molecules covalently bonded together vi a an amide bond (TPP-NHCO-SPFGraphene, Scheme 1 and 2) was carried out using an amine-functionalized prophyrin (TPP-NH_2) and Graphene oxide in N,N-dimethylformamide (DMF), following standard chemistry. Large-scale and water-soluble Graphene oxide was prepared by the modified Hummers method [24, 25]. Results of atomic force microscopy characterization have confirmed that this grapheme material can be easily dispersed at the state of complete exfoliation, which consists of almost entire single-layered Gra-
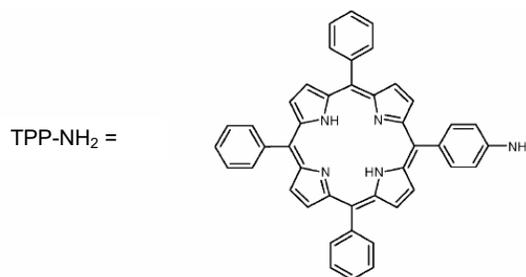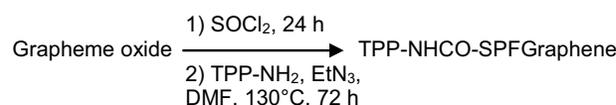
Scheme 1: *Synthesis scheme of TPP-NHCO-SPF Graphene [26].*
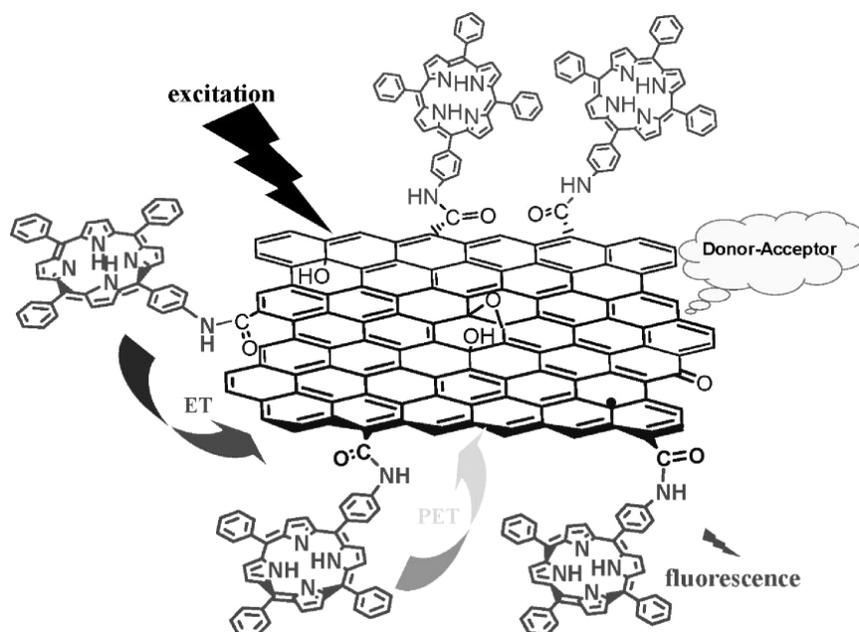
Scheme 2: *Schematic representation of part of the structure of the covalent TPP-NHCO-SPFGraphene [26].*

phene sheets in H_2O [24, 25]. TPP-NH_2 and Graphene oxide molecules are covalently bonded together by an amide bond. Much care has been taken to make sure all the unreacted TPP-NH_2 has been removed using extensive solvent washing, sonication, and membrane filtration. Details are given in the Experimental part. The attachment of organic molecules to Graphene oxide has made TPP-NHCO- SPFGraphene soluble in DMF and other polar solvents [24, 26].

2.2.2. Standard Mo solution
A standard solution of Mo(II), 1.0×10^{-3} M was prepared by dissolving 0.1111 g Mo nitrate (Merck) in water containing a drop of concentrated HCl and diluting to the mark in a 250 mL volumetric flask. All working solutions of Mo(II) were prepared by serial dilution of the stock solution.

2.2.3. Standard bromopyrogallol red solution
An aqueous solution of (1.0×10^{-4} M) bromopyrogallol red (Merck) was prepared by dissolving of 0.0140 g bromopyrogallol red in water and diluting to the mark in a 250 mL volumetric flask. Universal buffer solutions in the range from 2.0 to 10.0 were prepared with acetate, phosphate, and borate. Glycine/HCl buffer was used for pH 1.0. Stock solutions (5.0×10^{-3} M) of interfering ions were prepared by dissolving suitable

salts in water, hydrochloric acid or sodium hydroxide solutions.

2.3. General procedure
The column was packed with 3.0 g adsorbent and was conditioned with 1.0-2.0 mL of pH 5.0. Then, 10.0 mL of Mo solution (5.0×10^{-5} M) was passed through the column at 0.1 mL min^{-1}. The analyte was eluted from the column by 1.0 mL of HCl, 1.0 M. A sample solution was prepared by pouring 0.5 mL of buffer solution (pH 1.0) in a 10.0 volumetric flask and 3.0 mL of 1.0×10^{-4} M bromopyrogallol red was added. The mixture diluted to ca. 8 mL with water then 1.0 mL of Mo(II) (5.0×10^{-5} M) (eluted solution from column) was added and the solution diluted to the mark with water. The reaction mixture as agitated and then an appropriate amount of the solution was transferred to the spectrophotometric cell and variation in absorbance was recorded for the first 0.5-5.0 min from initiation of the reaction at 517 nm. A calibration graph was plotted with absorbance change ($\Delta A = A_5 - A_{0.5}$) versus Mo concentration.

3. RESULTS AND DISCUSSION

Organic-solution-processable functionalized-gra-

Int. J. Bio-Inorg. Hybd. Nanomat., Vol. 2, No. 4 (2013), 495-502

Moghimi A
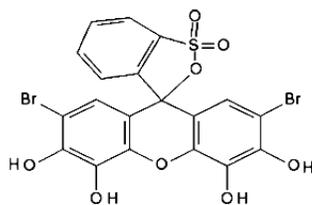
Figure 1: Structure of Bromopyrogallol red structure.

phene (SPFGraphene) with the following structure (Scheme 1) is a new chelating agent which can form stable complex with Mo(II). By immobilizing this tridentate bisamide ligand on microcrystalline naphthalene, Mo(II) can be adsorbed. Then desorption of Mo is carried out by using a strong inorganic acid. The Mo(II) concentrations were determined spectrophotometrically after passing solution through the column. Therefore, first the optimum conditions for spectrophotometric procedure should be studied.

3.1. Effect of variables on the determination of Mo

Bromopyrogallol red with following structure Figure 1 is oxidized by Mo and the absorbance of the solution decreases with time, at $\lambda = 517$ nm. The change in the signal is proportional to Mo concentration. Figure 3 shows the absorption spectra of bromopyr-ogallol red-Mo system at different times. Experiment (spetrophotometric determination) on eluted Mo solution

Figure 3: Effect of bromopyrogallol red concentration on the reaction rate. Conditions: pH 1.0; Mo(II), 1.0×10^{-5} M; temperature, 30°C; measuring time, 5.0 min from initiation of the reaction.

was done at different pH values (1.0-5.0). Figure 2 shows the effect of pH on the net absorbance (ΔA). The maximum net absorbance is at pH 1.0; whereas higher pH values cause decreasing in the signal. At higher pH values, oxidation potential of bromopyrogallol red increases, thus the reaction rate and ΔA decreased. Therefore the pH of 1.0 was selected for this study. The influence of bromopyrogallol red concentration on the reaction rate was tested at pH 1.0 with 1.0×10^{-5} M, Mo(II) at 30°C (Figure 3). It can be seen that the best concentration for bromopyrogallol

Figure 2: Effect of pH on the reaction rate. Conditions: bromopyrogallol red, 1.0×10^{-5} M; Mo(II), 1.0×10^{-5} M; temperature, 30°C; measuring time, 5.0 min from initiation of the reaction.
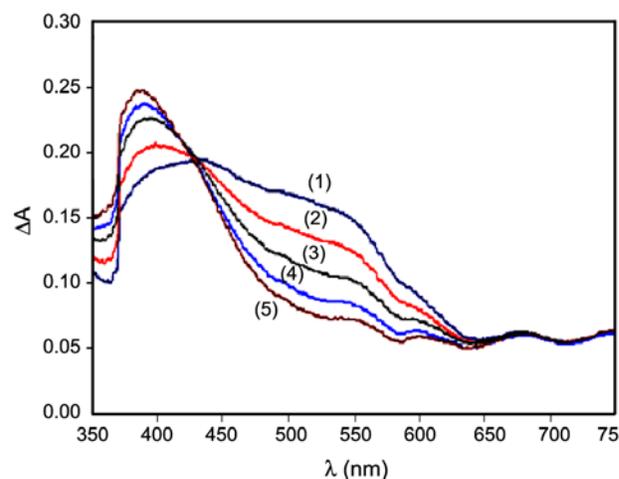
Figure 4: Effect of temperature on the rate of reaction. Conditions: pH 1.0; Mo(II), 1.0×10^{-5} M; bromopyrogallol red, 3.0×10^{-5} M; measuring time, 5.0 min from initiation of the reaction.

Moghimi A

Int. J. Bio-Inorg. Hybd. Nanomat., Vol. 2, No. 4 (2013), 495-502

red is 3.0×10^{-5} M. At higher values the aggregation of bromopyrogallol red causes the reaction rate to be decreased. Effect of temperature on the maximum signal (ΔA) was studied for the range of 10-50°C, under optimum conditions otherwise as previously described. Figure 4 shows that with increasing temperature up to 30°C, ΔA signal or the rate of reaction increases. So temperature was fixed at 30°C. At higher temperature bromopyrogallol red can be decomposed.

3.2. Effect of variables on the preconcentration

The effect of pH on preconcentration of Mo(II) was examined in range of 1.0-10.0, and the results are shown in Figure 5. The results show that in the pH range of 5.0-10.0, the analyte was adsorbed on microcrystalline naphthalene quantitate and the recovery was more than 90%. For pH lower than 5.0 the complex will not be formed on adsorbent (at acidic media, active sites of ligand will be protonated) and at high pH values, Mo will precipitate on the column (precipitating instead of adsorption will occur). In order to obtain the best conditions for determination after preconcentration and to prevent the precipitation of Mo (especially at high concentrations), the most acidic pH from this range of buffers (5-10), was selected. The influence of analyte retention time was investigated by passing 10.0 mL of Mo(II) (5.0×10^{-5} M) solution in the pH 5.0 with different flow rates, and performing the experiment with the passed solution. The results show that
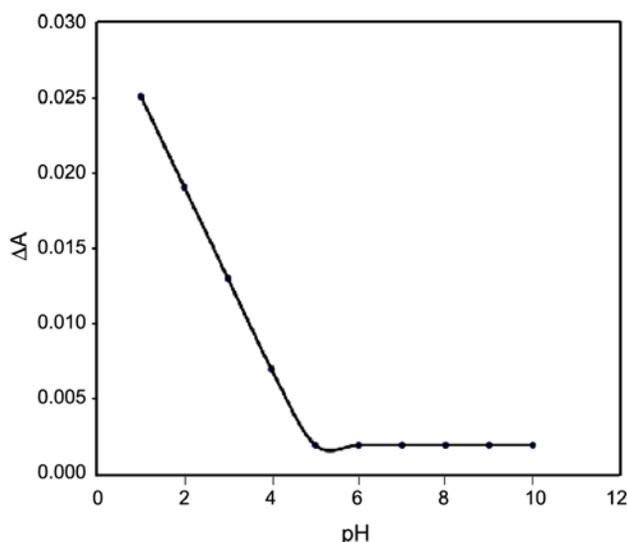
Figure 6: *Effect of HCl concentration for elution conditions: Mo(II), 5.0×10^{-6} M; Ph 1.0; HCl, 1.0 mL; optimum conditions for determination of Mo(II).*

in the higher flow rates, Mo cannot be adsorbed on microcrystalline naphthalene quantitatively. The best flow rate was selected to be 0.1 mL min^{-1}. As the Mo complex is unstable in high acidic solutions, hydrochloric acid was selected to desorb the adsorbed analyte. Figure 6 shows that Mo(II) can be desorbed from the adsorbent by elution with 1.0 mL, HCl, 1.0 M. For investigating the ability of microcrystalline naphthalene to adsorb Mo(II) after sequential elusions, the preconcentration process was repeated for many times. It was indicated that the results were satisfactory, even by using one column for 10 times, without changing the packing. The different volumes of Mo solution, 1.0×10^{-8} M in the range of 10-1000 mL were passed through the column and the signal of each eluted solution was compared with calibration curve data which is achieved from determination method. The obtained signals of concentrated Mo solutions presented that a preconcentration factor of 100 can be achieved by this method. The effect of ionic strength on the sensitivity was studied. The sensitivity would be slightly changed with increasing the ionic strength of the reaction mixture.

3.3. Retention capacity of the adsorbent

The retention capacity of organic-solution-processable functionalized-graphene (SPFGraphene) adsorbent was determined by a batch method. The 20 mL solution of Mo(II) 1.0×10^{-4} M in pH 5.0 was transferred into a separating funnel and 3 g adsorbent was

Figure 5: *Effect of pH on the preconcentration recovery. Conditions: Mo(II), 5.0×10^{-6} M; flow rate, 0.1 mL min^{-1}; optimum conditions for determination of Mo(II).*

Int. J. Bio-Inorg. Hybd. Nanomat., Vol. 2, No. 4 (2013), 495-502

Moghimi A

added. The separating funnel was shaken vigorously for 30 min. Concentration of Mo in the filtrate was determined according to calibration curve data and then adsorbed amount of Mo was calculated. The retention capacity (mg adsorbed Mo/ g adsorbent) was obtained to be 0.1672 mg g^{-1} of adsorbent or 2.01 mg g^{-1} of ligand.

3.4. Calibration graph, reproducibility and detection limit

A series of standard solutions of Mo(II) were treated under the above-mentioned optimized experimental conditions. Mo concentration can be determined in the range of 6.9×10^{-9} to 2.7×10^{-5} M with linear equation; $\Delta A = 0.00078 \times C + 0.0056$ and regression coefficient of $r^2 = 0.9988$ (ΔA is absorbance signal after precon-centration and C is molar concentration of Mo$\times$106). The experimental limit of detection is 1.78×10^{-9} M (S/N = 3). The relative standard deviation (R.S.D.%) for 10 replicate measurements of 5.0×10^{-9}, 1.0×10^{-8}, 1.0×10^{-7}, 3.0×10^{-6} and 1.0×10^{-5} M of Mo(II) were 3.04, 2.95, 2.11, 3.12 and 1.90%, respectively.

3.5. Influence of foreign ions

The influence of contaminant species presented in various samples on the determination of 5.0×10^{-6} M, Mo(II) was investigated. The tolerance limit was defined as the concentration of added ions, causing a relative error less than 3% (Table 1). Some metal cations can be adsorbed on microcrystalline naphthalene at different pH values. This proposed adsorbent is not only able to remove anions of the Mo(II) solution but also can decrease the interference of some cations. Some of important ions that can be found in the real

Table 1: Interferences effect on the determination of 5.0×10^{-6} M, Mo(II).

Tolerance limit ($W_{ion}/W_{Mo(II)}$)	Species
100	NH_4^+, Na^+, K^+, H_3BO_3, Hg^{2+}, Ba^{2+}, Cd^{2+}, Co^{2+}, Ca^{2+}, Pb^{2+}, Sn^{2+}, Sr^{2+}, Tl^+
48	Al^{3+}, Mg^{2+}, Cr^{3+}, Cu^{2+}
25	Fe^{2+}, Fe^{3+}
19	Zn^{2+}
1	Sb^{3+}, Ag^+

samples with Mo(II) such as Sn^{2+}, Hg^{2+}, Cd^{2+}, Co^{2+}, Ca^{2+}, Pb^{2+} and Tl^{1+} do not have any interference on the determination of Mo(II). Al and Fe can be troublesome in the determination procedure but with preconcentration their interference decreases.

The reported method is selective and simple and it has excellent capacity factor. Among other mentioned methods in Table 2 stripping voltammetry has a good sensitivity but it needs expensive apparatus and needs the operator to be skillful. Conventional solvent extractions are not sensitive enough and they consume a large amount of solvent. Also most of extracting solvents are toxic and volatile.

On the basis of the results obtained from the Mo(II) standards, the recommended preconcentration method has been successfully applied prior to spectrophtomeric determination of low values of Mo in the tap water

Table 2: Comparison of some methods for preconcentration and determination of thallium with proposed method.

Reference	LDR (ng mL^{-1})	DL (ng mL^{-1})	Method
[21]	3.75–17.8	1	Solid–liquid extraction
[22] [20]	0.1–100 5–250	0.08 1	Potentiometric stripping
[23] [24] –	5–20 40–18000 2.1–2000	4 20 0.3	Liquid–liquid extraction Microcrystalline naphthalene Proposed method

Table 3: *Spectrophotometric of Mo(II) in the real samples after preconcentration.*

Recovery %	ICP	Found (×10⁻⁸ M)	Added (×10⁻⁸ M)	Sample
–	-	–	–	
98.5	1.05 ± 0.09	1.09 ± 0.089	1.0	
97.3	4.95 ± 0.55	4.98 ± 0.079	5.0	Drinking water
98.3	8.02 ± 0.10	7.90 ± 0.069	8.0	
98.5	10.41 ± 0.07	10.39 ± 0.016	10.0	
–	–	–	–	
99.6	0.95 ± 0.19	0.99 ± 0.080	1.0	
98.6	4.80 ± 0.08	4.78 ± 0.075	5.0	River water
95.7	7.930 ± 0.10	7.68 ± 0.094	8.0	
98.8	9.95 ± 0.08	10.47 ± 0.076	10.0	

Table 4: *Analytical characteristics of organic-solution-processable functionalized-graphene (SPFGraphene) for determination of Mo(II).*

Parameter	Analytical feature
Linear range (M)	10^{-9} to $2.7×10^{-5}×6.9$
r^2	0.9988
Limit of detection (ng L⁻¹) (3σ, n = 10)	10^{-9} M×1.78
Repeatability (R.S.D.[a], %) (n = 10)	3.0
Enrichment factor[b]	122
Enhancement factor	100
Sample volume (mL)	10.00
Extraction time (min)	<4

[a] *Mo(II) concentration was 20 nM for which R.S.D. was obtained;* [b] Enhancement factor is the slope ratio of calibration graph after and before extraction.

(Tehran, taken after 10 min operation of the tap), rain water (Tehran, 22 January, 2013) samples. The analysis was performed by using the standard addition technique. The results are summarized in Table 3. Good recoveries in all samples were obtained. This method was reliable through comparing with each other [24-26]. Table 4 summarizes the analytical characteristics of the optimized method, including linear range, limit of detection, reproducibility, and enhancement factor. The calibration graph was linear in the range of $6.9×10^{-9}$ to $2.7×10^{-5}$ M of Mo. The limit of detection, defined as CL = 3 SB/m (where CL, SB and m are the limit of detection, standard deviation of the blank and slope of the calibration graph, respectively), was

$1.78×10^{-9}$ M. The precision, expressed as relative standard deviation of three measurements is better than 3.0%. The enhancement factor was obtained from the slope ratio of calibration graph after and before extraction, which was about 100.

4. CONCLUSIONS

Solid-liquid extraction with microcrystalline naphthalene is an effective separation and preconcentration technique for trace elements. The method has the advantages of being simple, inexpensive and selective this proposed preconcentration method has a high en-

richment factor (100) which develops possibility of determining concentration levels as low as sub micro amounts of Mo with eliminating the interference of some diverse ions. The selected determination procedure (after preconcentration) is convenient, sensitive and fairly selective.

ACHNOWLEDGMENTS

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