Extraction of Trace amounts of Mo(II) in water samples using Nano Graphene oxide modified with porphyrinand determination FAAS

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Abstract— **A simple, highly sensitive, accurate and selective method for determination of trace amounts of Mo^{2+}in water samples .In this paper, a Graphene oxide with covalently linked porphyrin (GO–H_2P) based new sorbent was prepared. The modified Graphene oxide (GO–H_2P) was used for preconcentration of Mo(II) from aqueous solutions. The analytical variables were optimized by central composite design (CCD). Flame atomic absorption spectrometer was utilized for determination of Mo(II). The analytical features for sorption were found to be 5.2; 4.3 mL min^{-1} and 55.0 mL for pH, flow rate and sample volume, respectively. HNO_3 was used as eluent and maximum preconcentration factor was found to be 200.Elution parameters were also determined as 4 mL min^{-1}; 0.6 mol L^{-1} and 5.1 mL forflow rate, eluent concentration and eluent volume, respectively.Limit of detection and limit of quantification were found to be 49.6 and 163.7 ng L^{-1}, respectively. Validation of the developed method was performed using certified reference material (TMDA-53.3). The methodology was applied for determination of Mo(II) in natural water samples and satisfactory results were obtained.**

Index Terms— **Graphene oxide with covalently linked porphyrin (GO–H_2P), preconcentration, Cadmium, Central Composite Design, Flame Atomic Absorption Spectrometer, water.**

I. INTRODUCTION

Mo 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, Mo can bind to the cell membrane and hinder the transport process through the cell wall. Mo at nearly 40ng mL^{-1} is required for normal metabolism of many living organisms [9, 10]. On the other hand, Mo 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 Mo is usually carried out by flame and graphite furnace atomic absorption spectrometry (AAS) [11, 12,] as well as spectrometric methods [13, 14-18] .However, due to the presence of Mo 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.

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Recently, Solid-phase extraction (SPE) is the most common technique used for preconcentration of analytes in environmental water because of its advantages of high enrichment factor, high recovery, rapid phase separation, low cost, low consumption of organic solvents and the ability of combination with different detection techniques in the form of on-line or off-line mode [19,20-33].
 Solid phase extraction (SPE) or liquid-solid extraction is poplar 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 Mo 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 Mo^{2+} in low concentration. The structure of Graphene oxide with covalently linked porphyrin(GO–H_2P)is shown in Scheme 1. The chelated ions were desorbed and determined by FAAS. The modified solid phase could be used at least 50 times with acceptable reproducibility without any change in the composition of the sorbent, GO–H_2P. On the other hand, in terms of economy it is much cheaper than those in the market, like C_{18} SPE mini-column.

In the present work, Graphene oxide with covalently linked porphyrin (GO–H_2P) was employed for production of solid phase. The synthesized and characterized new sorbent (GO–H_2P)was utilized for preconcentration of Mo(II) from water samples. Determination of Mo(II) concentration was achieved by FAAS after preconcentration procedure. The experimental conditions were optimized by CCD.

II. EXPERIMENTAL

A. Reagents and Chemicals

The analytical grade deionized water was obtained by reverse osmosis system. All containers and glassware were kept overnight in 10% nitric acid and rinsed three times with water before use.1,000 mg L-1stock Mo(II) standard solution was
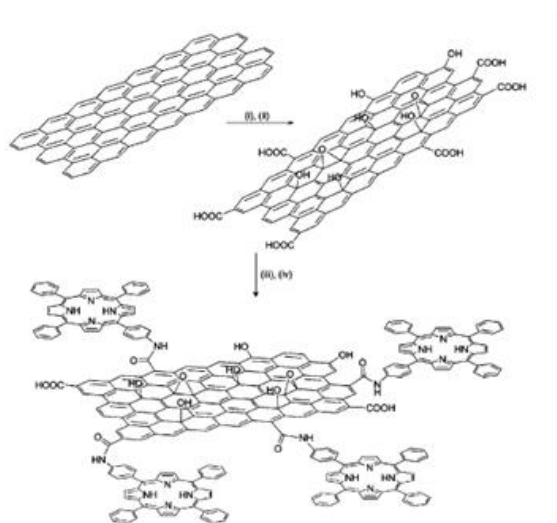
prepared from $Mo(NO_3)_2.4H_2O$ (Merck) and diluted as required to the $\mu g\ L^{-1}$ levels. In interference study, cations were added as nitrates and the anions were added as sodium salts. Feasibility of the suggested method was tested with Lake Ontario water certified reference material (TMDA-53.3, lot 0310).

Synthetic procedures
Preparation of GO–H_2P

GO (15 mg) was stirred in 20 mL of oxalyl chloride at 80 °C for 24 h to activate the carboxylic units by forming the corresponding acyl chlorides. Then, the reaction mixture was evaporated to remove the excess oxalyl chloride and the brownish remaining solid (GO–COCl) was washed with anhydrous tetrahydrofuran (THF). After centrifugation, the resulting solid material was dried at room temperature under vacuum. For the covalent coupling between the free amino function of H_2P and the acyl chloride of GO, 15 mg of GO–COCl was treated under anaerobic, dry conditions with 7 mg of H2P dissolved in 6 ml of dry THF at room temperature for 72 h. The hybrid material, namely GO–H_2P, was obtained as a brown-graysolidby filtration of the reaction mixture through 0.2 mm PTFE filter and the filtrate was sufficiently washed with methylene chloride ($4\times$ 20 ml) to remove non-reacted free H_2P and then with diethyl ether (2×20 mL) before being dried under vacuum.

Scheme 1 A schematic illustration for the preparation of GO with covalently linked H_2P. (i) H_2SO_4/HNO_3 (2 : 1 v/v), (ii) $KClO_3$, 96 h, (iii) $(COCl)_2$,80 °C, 24 h, (iv) 5-(4-aminophenyl)-10,15,20-triphenyl-21,23H-porphyrin, THF, r.t., 72 h.

B. Apparatus

A Philips X Pert-Pro diffracrometer (Mo Kα λ=1.54060 A°, 30 mA, 40 kV), and Perkin Elmer Spectrum 65 FTIR-ATR spectrometer were used to confirm the synthesized GO–H2P.Determination of Mo(II) in solutions were carried out by Perkin Elmer AAnalyst200FAASequipped with deuterium background correction. All measurements were performed inan air/acetylene flame. GFL 3005 orbital shaker having speed and time control was used forpreparation of the

sorbent. During the solid phase extraction experiments, VelpScientificaSP311 peristaltic pump with Tygon tubes was used. A Thermo Orion 5 Star model pH meter,Heidolph MR 3001 K model magnetic stirrer, Sartorius TE214S electronic balance,Eppendorf Research micro pipettes wereused for the present work.Funnel tipped glass tube(10x100 mm) equipped with stopcock was used as a column for the preconcentrationexperiments.

C. Preparation of Solid Phase

The commercially available Graphene oxide with covalently linked porphyrin (GO–H2P) was activated by refluxing with 0.5 mol L^{-1} HNO_3 for 1 h to remove any adsorbed metal ions. Then it was filtered, washed with deionized water until the filtrate was neutral.

In order to synthesize physically bonded GO–H2P, 10.0 g of Graphene oxide with covalently linked porphyrin (GO–H2P) was added to 50.0 mL acetone containing 50 mg MSE and refluxed for 24 h. The product was filtered off and washed with deionized water and dried at room temperature.

D. General Enrichment Procedure

1.0 g of GO–H2P was filled in the column and the effective factors on the preconcentration including pH, flow rate andselection of eluent type were investigated using the model solutions containing 5μg Mo(II). The determination of Mo(II) in eluates were achieved by FAAS. According to the precipitation of the metal hydroxides at alkaline environment, pH effect was evaluated within the range of 3-7. Experiments of flow rate for sorption and elution were performed at 3-20 mL min^{-1}. In order to choose a proper eluent for desorbing the Mo(II) from the sorbent surface, different mineral and organic acids were tested .The proposed analytical procedure for Mo(II)preconcentration was optimized using three level full factorial CCD. The optimization procedure was performed separately for sorption and elution. Three variables; pH, sample volume, flow rate and eluent volume, eluent concentration, flow rate were regarded as factors for sorption and for elution, respectively.

III. RESULTS AND DISCUSSION

The treatment of Graphene oxide with covalently linked porphyrin (GO–H_2P) can lead to the derivatization of both the edge carboxyl and surface hydroxyl functional groups via formation of amides [20] or carbamate esters [21], respectively.

The formation of GO–H_2P was followed by ATR-IR spectroscopy.Initially, in the spectrum of GO, the carbonyl vibration appears at 1716 cm^{-1}, while there are fingerprints at 3616 cm^{-1} and 3490 cm^{-1} due to the presence of hydroxyl species at the basal plane of graphene. The covalent linkage of H_2P with the acyl chloride activated GO is evident from the presence of a band at 1630 cm^{-1}, which is characteristic for the carbonyl groups of the amide units[23].
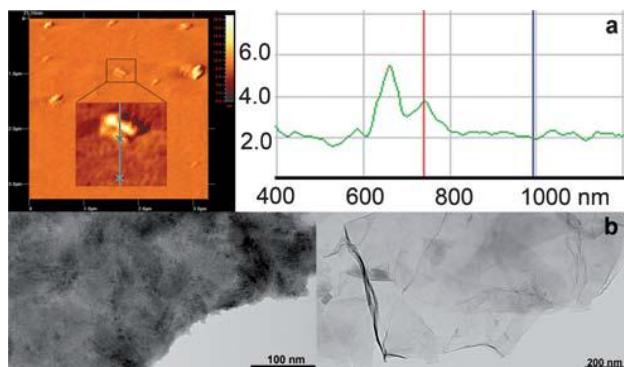
Fig. 1 (a) Representative AFM image of GO–H_2P and profile analysis showing a height of 1.77 nm for the enlarged region. Section analysis of other regions of the image show height ranges of 1.5–3.5 nm. (b) TEM images of the intact graphite (left panel) and GO–H_2P hybrid material (right panel).

The amount of porphyrin attached onto the graphene sheet was evaluated by thermogravimetric analysis. As compared with the TGA results of pure graphite, which is thermally stable up to 900 °C under nitrogen, and GO which decomposes above 600 °C,after having lost the oxygenated species at 240 °C (i.e. 14.7% weight loss), the 6% weight loss occurred in the temperature range 250–550 °C for the GO–H_2P material, is attributed to the decomposition of H2P (Fig. 2).
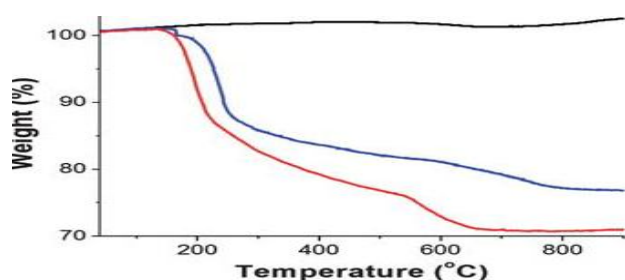

Fig. 2. The TGA graphs of graphite (black), GO (blue) and GO–H_2P (red), obtained under an inert atmosphere.

The GO–H_2P material forms a stable dispersion in DMF at a concentration not exceeding 1 mg mL^{-1}. The electronic absorption spectrum of GO–H_2P in DMF (Fig. 3), shows (i)a broad signal monotonically decreasing from the UV to the visible region, which is attributed to GO and (ii) a characteristic band at 420 nm (Soret-band) corresponding to the covalently grafted H_2P units (the Q-bands at 516, 557, 589 and 648 nm wereflattened to the base line in the GO–H_2P material). Interestingly, the absorption of porphyrin in the GO–H_2P material is broadened, shortened and bathochromically shifted (ca. 2 nm) as compared to that of the free H_2P, a result that corroborates not only the linkage of porphyrin with the GO sheets but also electronic interactions between the two species (i.e. GO and H_2P) in the ground state. These results are in agreement with studiesbased on other hybrid systems consisting of porphyrins covalently grafted to carbon nanotubes and nanohorns[20].
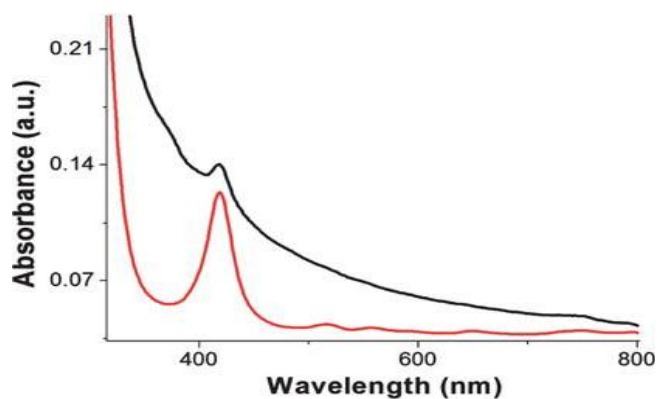

Fig. 3 .The UV-vis spectra of GO–H_2P (black) and free H_2P (red),obtained in DMF.

A. Effect of pH

The pH of the sample solution plays important role in retention of metals on sorbent. The pH of the model solutions containing 5μg Mo(II) were adjusted to certain value using diluted HNO3 and NaOH. As shown in Fig. 4,the recovery results were not dramatically affected by the change in pH between 4 and 7.According to this, pH=2.9 was chosen as center value for the optimization procedure.

B. Desorption Reagent

0.5 mol L^{-1} of HNO_3, HCl, CH_3COOH, H_2SO_4 and H2O2 were tested for desorption of Mo(II) from GO–H2P. The recovery percentages were varied between 5.7-87.9 % except HNO_3 elution experiments.It was observed that HNO3is the best as an eluent and the recovery percentage is 94.2±1.5 %.

C. Effect of Flow Rate on Sorption and Elution

The retention of a metal ion on the sorbent also depends on the flow rate of the sample solution. Thus, the both effect of flow rate of the sample and eluent on the sorption and desorption of Mo(II) ions were investigated between 3-20 mL min^{-1}. Quantitative results (> 95%) were obtained up to 10 and 8 mL min-1 for sorption and elution, respectively. In order to avoid an abrupt change in adsorption and increase the contact time of the sample solution with the sorbent,flow rate was selected as 4 mL min^{-1} for sorption and elution.

D. Optimization of Variables

Optimization of the preliminary studies was achieved by a three level full factorial CCD with20 runs.Table 1lists the maximum, minimum andcentervaluesof the variables for sorptionand elution. The metal concentration in solutions was determined with external standardcalibration method by FAAS. The experimental design matrix and the results for sorptionand elution are given in Table 2and 3.Quadratic Eq. (1) and Eq. (2), which were obtained byusing data of response values, are given below for sorption and elution, respectively.

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$$y = 0.512149 - 0.72568x_1 - 0.70171x_2 - 0.98307x_3 + 0.056576x_1^2 + 0.171216x_2^2 + 0.493081x_3^2 + 1.565725x_1x_2 + 1.556098x_1x_3 + 1.606563x_2x_3 \qquad (1)$$

$$y = 0.683354 + 0.018073x_1 + 1.220284x_2 + 0.130563x_3 - 0.576576x_1^2 + 1.235323x_2^2 - 0.33237x_3^2 + 0.071216x_1x_2 - 0.06881x_1x_3 - 0.07098x_2x_3 \qquad (2)$$

x_1, x_2 and x_3 represents the 1st, 2nd and 3rd factors. Derivatives of the equations in terms of x_1, x_2 and $x_3$were equalized to zero and solved using Microsoft®Excel.The real values presented in Table 4 obtained from CCD and used as optimal conditions for further experiments.

E. Interference Effects

The preconcentration procedures of trace metal ions can be strongly affected by other ions. For this reason, the effects of matrix ions were investigated under optimal conditions. The results revealed that the GO–H_2P behaves as a neutral ionophore in the pH range 3.0 [49,50] so that the Mo(II) ions are retained as ion pair complexes by the membrane disks. As seen, acetate ion is the most efficient counter anion for the SPE of Mo(II) ions. The influence of the concentration of sodium acetate ion on Mo(II) recovery was investigated, and the results are shown in Table 4. As seen, the percent recovery of Mo^{2+} increasedwith the acetate concentration until a reagent concentration of about 0.1 M is reached, beyond which the recovery remained quantitative.Moreover, acetate ion acts as a suitable buffering agent, while it effectively contributes to the ions- pair formation; thus, in the SPE experiments, there was no need for the addition of any buffer solution.The tolerance limit of coexisting ions was given in Table 5.The experiments indicated that, no further sample treatment or masking reagents are needed.

F. Effect of Sample Volume

The preconcentration studies were applied to solutions within the range of 25-1000 mLcontaining 5 μg amount of Mo(II) to explore the possibility of enriching at low concentrationwith high enrichment factor. The recovery value was obtained as 98.7 % at 1000 mL samplevolume by analyzing 5 mL eluate and the highest preconcentration factor was found to be200.

G. Analytical Figures of Merit

The accuracyand precision (RSD, %)of the proposed solid phase extraction procedure underoptimal conditions were investigated (n=10) as 102.0±0.2 % and 2, respectively. Limits ofdetection (LOD) and the limits of quantification (LOQ) were obtained by using a criterionsignal-to-noise ratio of 3 and 10, respectively. The results were calculated 49.6ng L^{-1}forLOD and 163.7ng L^{-1} for LOQ.

H. Validation and Application of the Improved Method

The developed procedure was validated by Mo (II) determination in certified referencematerial.The results are given in Table 6. A statistical evaluation was performed by Student'st test and t value was calculated as 2.95. Critical$t$value (4.30) is higher than the calculatedone at 95 % confidence level. This test showed no significant difference between Mo(II)concentration obtained from the presented method and the certified value.

I. Real Sample Analysis

To assess the applicability of the method to real samples, it was applied to the extraction and determination of Mo(II) from different water samples. Tap water(Tehran, taken after 10 min operation of the tap),rain water(Tehran, 20 January, 2014), Snow water (Varamin , 6 February ,2014)and Sea water(taken from Caspian sea, near the Mahmoud-Abad shore) samples were analyzed(Table 7). As can be seen from Table 4 the added Mo(II) ions can be quantitatively recovered from the water samples used. As is seen, the recovered Mo(II) ion reveals that the results are quite reliable and are in satisfactory agreement with those obtained by ICPAES (Tables 7).

IV. CONCLUSION

In the present study, a new sorbent is prepared by using Graphene oxide with covalently linked porphyrin (GO–H_2P) and for preconcentration of Mo(II) from natural water samples. The modified Graphene oxide with covalently linked porphyrin (GO–H_2P) was prepared easily and sorbedMo(II) rapidly. The preconcentration parameters pH, flow rate and sample volume for sorption procedure was obtained by CCD as 5.2, 4.3 mL min-1, 55.0 mL, respectively. Elution parameters, flow rate, eluent concentration and eluent volume were also obtained as 4.1 mL min^{-1}, 0.6 mol L^{-1} and 5.1 mL, respectively. Enrichment factor was found to be 200 when 1000 mL of water sample(included 5μg) passed through the GO–H2P column. The interference effects of some ions were also investigated according to the improved method. The tolerance limits were between750-10,000 times greater as can be seen in Table 5. The mean recovery values for spiked water samples were satisfactory and confirmed the validity of the method. Additionally, mean %RSD value was 2 and showed that the precision of the method is quite good. Preconcentration factor, LOD, RSD, eluent type and concentration and detection technique of present work was compared with literature data in Table 8. In most cases, suggested method for Mopreconcentration with GO–H2P is comparable to, or better than, some of the previously reported Graphene oxide with covalently linked porphyrin (GO–H_2P) based modified adsorbents. Finally, the proposed method can be suggested as simple, sensitive, acMorate and repeatable method for determination of Mo(II) after preconcentration. This new enrichment procedure can also be applied to some other metal ions.

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