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Research Article

SOLID PHASE EXTRACTION OF TRACE CD(II) IN INDUSTRIAL WASTE WATER SAMPLE USING NANO GRAPHENE OXIDE AND DETERMINATION BY FLAME ATOMIC ABSORPTION

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ABSTRACT

Graphene oxide is a derivates of graphene that has a ultrahigh specific surface space with variety of chemically reactive functionalities, such as epoxy and hydroxyl groups on the basal plane and carboxylic acid groups along the area edge, which can be use different groups for functionalization, consequently it has a great promise for use as sorbent materials.A simple, highly sensitive, accurate and selective method for determination of trace amounts of Cd(II)in water samples .In this paper, a nano Graphene oxide with covalently linked porphyrin (GO–H_2P) based new sorbent was prepared. The modified nano Graphene oxide (GO–H_2P) was used for preconcentration of Cd(II) from aqueous solutions. The analytical variables were optimized by central composite design (CCD). Flame atomic absorption spectrometer was utilized for determination of Cd(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 for flow 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 Cd(II) in natural water samples and satisfactory results were obtained.

Keywords: *Nano Graphene Oxide with Covalently Linked Porphyrin (GO–H_2P), Preconcentration, Cd(II), Central Composite Design, Flame Atomic Absorption Spectrometer, Water*

INTRODUCTION

Graphenes are attracting renewed interests owing to recent advances in micromechanical exfoliation and epitaxial growth methods that make macroscopic 2D sheets of sp^2-carbon atoms available (Geim). A variety of simple yet elegant physics relating to its zero-gap semiconductor character has thus been demonstrated (Zhang). It would be very desirable to make these materials solution (or more accurately, dispersion) processable by coating or printing, which will open applications for large and/or flexible substrates. Graphite oxide (GO) is a possible candidate for this because it is a precursor to graphene through deoxidation either thermally or by chemical reduction (Lerf). Although GO itself has been studied for over a century (Brodie).

Its structure and properties remain elusive, and progress has been made only recently to give materials with limited dispersability and electronic quality (Eaton). Copper at trace concentrations acts as both a micronutrient and a toxicant in marine and fresh water systems (Lerf).

The direct determination of trace metals especially toxic metal ions such as Cu(II), tin, arsenic, lead, antimony and selenium from various samples requires mostly an initial and efficient pre-concentration step (Leyden (a),; Takeshima,; Taylor,). This pre-concentration is required to meet the detection limits as well as to determine the lower concentration levels of the analyte of interest. This can be performed simply in many ways including liquid and solid phase extraction techniques (Nambiar,. Caroli,). The application of solid phase extraction technique for pre- concentration of trace metals from different samples results in several advantages such as the minimal waste generation, reduction of sample matrix effects as well as sorption of the target species on the solid surface in a more stable chemical form (Alexandrova).

The normal and selective solid phase extractors are those derived from the immobilization of the organic compounds on the surface of solid supports which are mainly polyurethane foams (Arpadjan), filter paper (Leyden), cellulose (Gennaro) and ion exchange resins (Grote). Silica gel, alumina, magnesia and zirconia are the major inorganic solid matrices used to immobilize the target organic modifiers on their surfaces (Unger) of which silica gel is the most widely used solid support due to the well documented thermal, chemical and mechanical stability properties compared to other organic and inorganic solid supports (Boudreau). The surface of silica gel is characterized by the presence of silanol groups, which are known as weak ion exchangers, causing low interaction, binding and extraction of the target analytes (Kvitek). For this reason, modification of the silica gel surface with certain functional groups has successfully been employed to produce the solid phase with certain selectivity characters (Bruening and Moghimi, 2013). Two approaches are known for loading the surface of solid phases with certain organic compounds and these are defined as the chemical immobilization which is based on chemical bond formation between the silica gel surface groups and those of the organic modifier, and the other approach is known as the physical adsorption in which direct adsorption of the organic modifier with the active silanol groups takes place (Unger). Selective solid phase extractors and pre-concentrators are mainly based on impregnation of the solid surface with certain donor atoms such as oxygen, nitrogen and sulfur containing compounds (Mahmoud, a; Mahmoud b; Tong; Dadler). The most successful selective solid phases for soft metal ions are sulfur-containing compounds, which are widely used in different analytical fields. Amongst these sulfur-containing compounds are dithiocarbamate derivatives for selective extraction of Cd(II) (Mahmoud, a; Mahmoud b) and pre-concentration of various cations (Leyden (b), 1976; Narin *et al.*, 2009; Moghimi, 2008; Thurman *et al.*, 2006; Moghimi *et al.*, 2007; Moghimi *et al.*, 2006; Moghimi, 2007) and 2- mercaptobenzothiazol-modified silica gel for on-line pre-concentration and separation of silver for atomic absorption spectrometric determinations (Qiaosheng *et al.*, 1998). Ammonium hexa-hydroazepin-1-dithiocarboxylate (HMDC)-loaded on silica gel as solid phase pre-concentration column for atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) was reported (Alexandrova). Mercapto-modified silica gel phase was used in pre-concentration of some trace metals from seawater (Moghimi *et al.*, 2010). Sorption of Cu(II) by some sulfur containing complexing agents loaded on various solid supports (Tajodini) was also reported. 2-Amino-1- cyclopentene-1-dithiocaboxylic acid (ACDA) for the extraction of silver(I), Cd(II) and palladium(II) (Moghimi *et al.*, 2009), 2-[2-triethoxysilyl-ethylthio] aniline for the selective extraction and separation of palladium from other interfering metal ions (Narin) as well as thiosemicarbazide for sorption of different metal ions (Campderros) and thioanilide loaded on silica gel for pre-concentration of palladium(II) from water (Narin) are also sulfur contaning silica gel phases.

In our knowledge, SPE and preconcentration by Cd(II)-imprinted diazoaminobenzene–vinylpyridine copolymer packed-bed columns have not been employed for the separation and preconcentration of Cd(II) from aqueous solution. This paper reports the synthesis of Cd(II) imprinted and non-imprinted copolymers by copolymerizing Cdmium chloride (or without it), diazoaminobenzene (DAAB) and vinylpyridine (VP) using ethyleneglycoldimethacrylate (EGDMA) as cross-linker in presence of 2,2'-azobisisobutryonitrile as initiator and its analytical applications for column preconcentrative separation of Cd(II) from natural water.

In the present work, nano 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 Cd(II) from water samples. Determination of Cd(II) concentration was achieved by FAAS after preconcentration procedure. The experimental conditions were optimized by CCD.

Experimental

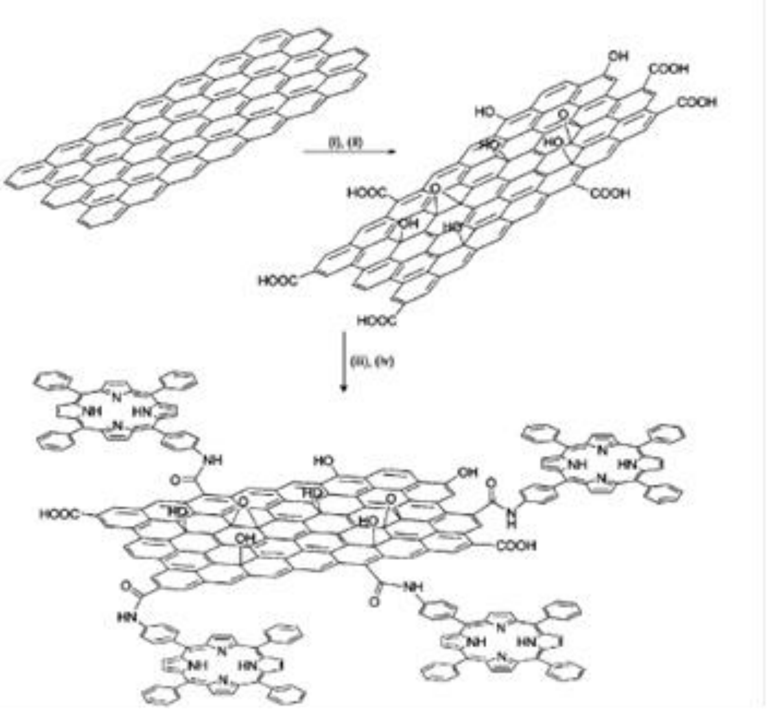
Reagents and Chemicals

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 Cd(II) standard solution was prepared from $Pb(NO_3)_2$. $4H_2O$ (Merck) and diluted as required to the µg 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× 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-21,23*H*-porphyrin, THF, r.t., 72 h

Apparatus

A Philips X Pert-Pro diffracrometer (Pb Kα λ=1.54060 A°, 30 mA, 40 kV), and Perkin Elmer Spectrum 65 FTIR-ATR spectrometer were used to confirm the synthesized GO–H_2P.Determination of Cd(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 preconcentration experiments.

Preparation of Solid Phase

The commercially available nano Graphene oxide with covalently linked porphyrin (GO–H_2P) 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–H_2P, 10.0 g of nano 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.

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 and selection of eluent type were investigated using the model solutions containing 5µg Cd(II). The determination of Cd(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 Cd(II) from the sorbent surface, different mineral and organic acids were tested .The proposed analytical procedure for Cd(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.

RESULTS AND DISCUSSION

The treatment of Graphene oxide with covalently linked porphyrin (GO–H_2P) can Cd(II) to the derivatization of both the edge carboxyl and surface hydroxyl functional groups via formation of amides (Karousis) or carbamate esters (Smith), 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 (Cataldo).

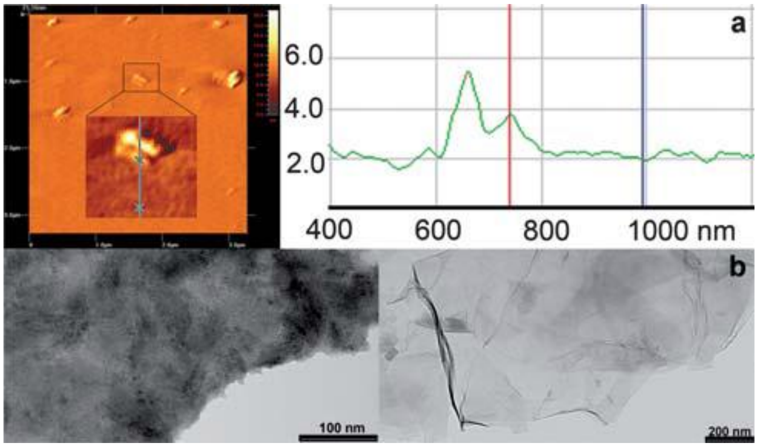


Figure 1: (a) Representative AFM image of GO–H_2P and profile analysis showing a height of 1.77 nm for the enlarged region. Section analysis of other regions of the image show height ranges of 1.5–3.5 nm. (b) TEM images of the intact graphite (left panel) and GO–H_2P hybrid material (right panel)

The amount of porphyrin attached onto the nano 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 H_2P (Figure 2).

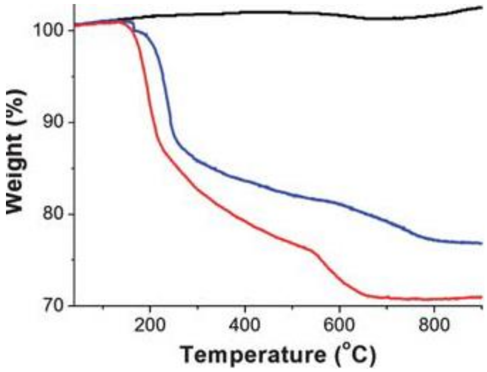


Figure 2: The TGA graphs of graphite (black), GO (blue) and GO–H_2P (red), obtained under an inert atmosphere

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 (Figure 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 were flattened 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 studies based on other hybrid systems consisting of porphyrins covalently grafted to carbon nanotubes and nanohorns (Karousis).

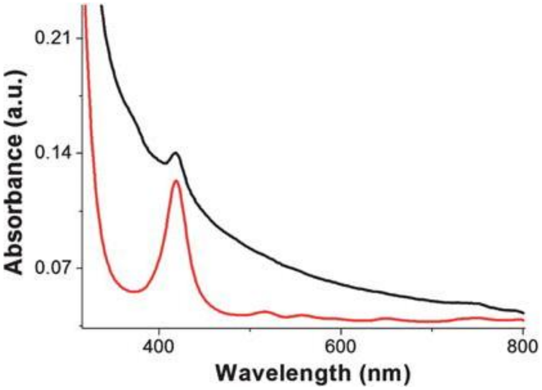


Figure 3: The UV-vis spectra of GO–H_2P (black) and free H_2P (red), obtained in DMF

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 Cd(II) were adjusted to certain value using diluted HNO_3 and NaOH. As shown in Figure 4, the recovery results were not dramatically affected by the change in pH between 4 and 7.According to this, pH=2.9 were chosen as centre value for the optimization procedure.

Desorption Reagent

0.5 mol L^{-1} of HNO_3, HCl, CH_3COOH, H_2SO_4 and H_2O_2 were tested for desorption of Cd(II) from GO–H2P. The recovery percentages were varied between 5.7-87.9 % except HNO_3 elution experiments. It was observed that $HNO_3$is the best as an eluent and the recovery percentage is 94.2±1.5 %.

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 Cd(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.

Optimization of Variables

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

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

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

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.

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 (Zelder) so that the Cd(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 Cd(II) ions. The influence of the concentration of sodium acetate ion on Cd(II) recovery was investigated, and the results are shown in Table 4.

As seen, the percent recovery of Pb^{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.

Effect of Sample Volume

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

Analytical Figures of Merit

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

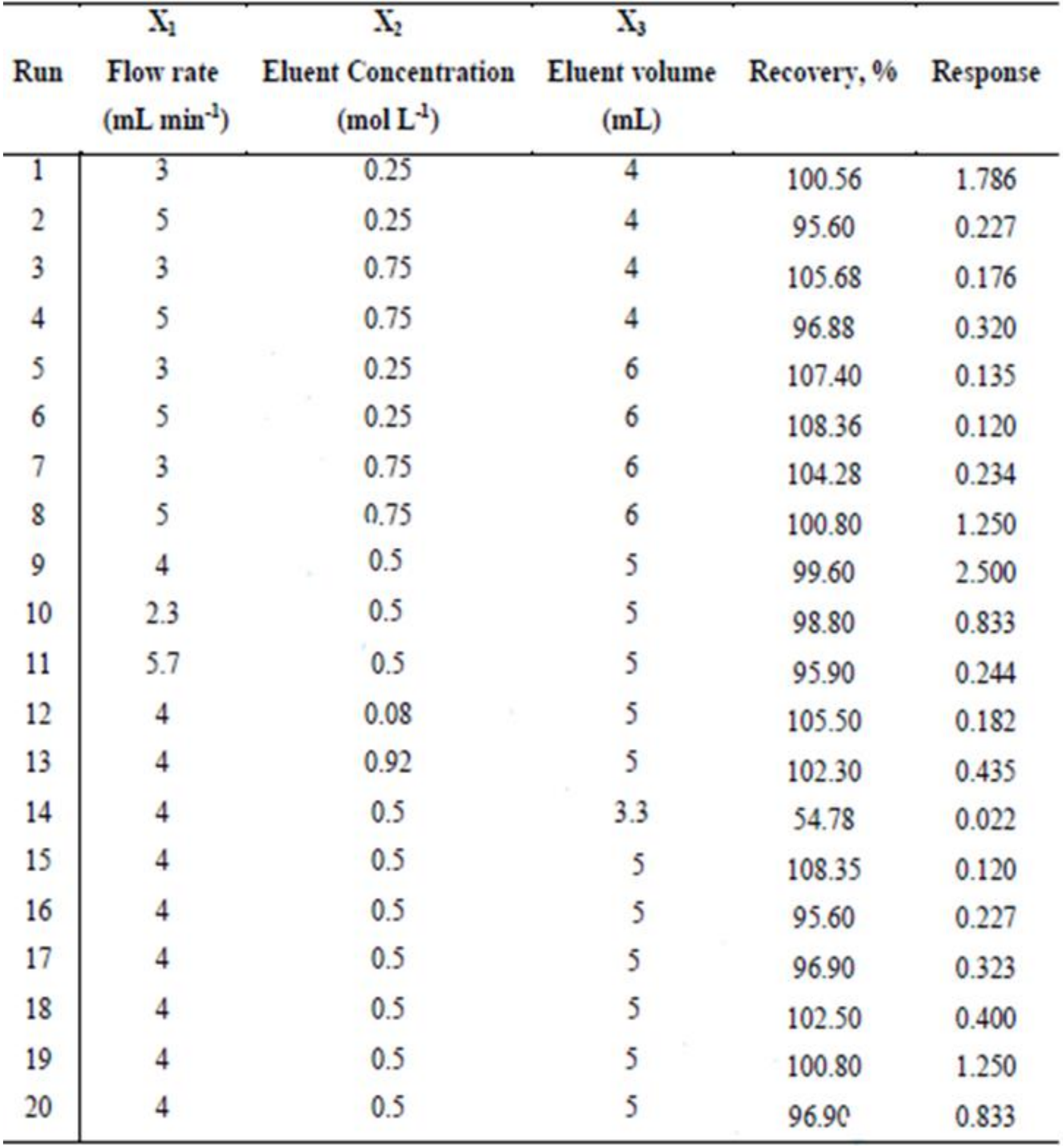
Table 1: Levels and the real values of factors utilized in CCD

Factors	*for sorption* Levels					Factors	*for elution* Levels				
	-α	-1	0	+1	+α		-α	-1	0	+1	+α
pH	3.3	4	5	6	6.7	Flow rate (mL min^{-1})	2.3	3	4	5	5.7
Flow rate (mL min^{-1})	2.3	3	4	5	5.7	Eluent Concentration (mol L^{-1})	0.08	0.25	0.50	0.75	0.92
Sample volume (mL)	8.0	25	50	75	92.0	Eluent Volume (mL)	3.3	4	5	6	6.7

Table 2: Experiments and recovery values for the sorption of Cd(II)

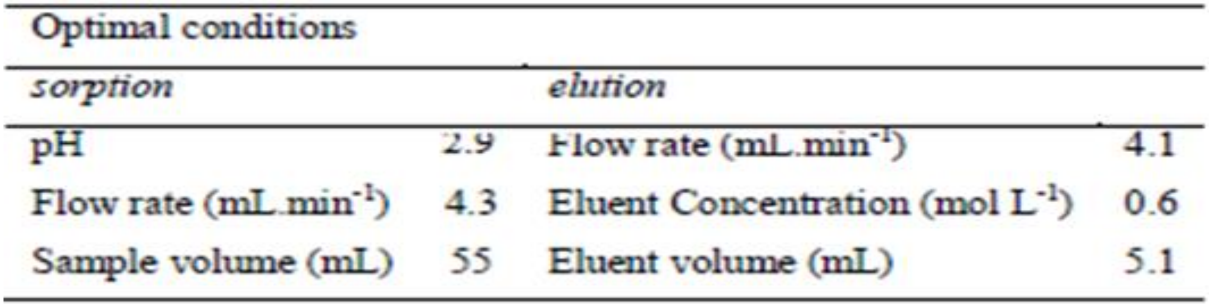
Run	X_1 pH	X_2 Flow rate (mL min^{-1})	X_3 Sample volume (mL)	Recovery, %	Response
1	4	3	25	99.91	11.636
2	6	3	25	104.58	0.218
3	4	5	25	112.41	0.081
4	6	5	25	82.40	0.057
5	4	3	75	113.56	0.074
6	6	5	75	13.10	0.012
7	4	5	75	113.47	0.074
8	6	5	75	99.30	1.420
9	5	4	50	100.62	1.623
10	3.3	4	50	81.40	0.054
11	6.7	4	50	72.30	0.036
12	5	2.3	50	96.00	0.250
13	5	5.7	50	81.91	0.055
14	5	4	8.0	99.56	2.272
15	5	4	92.0	99.30	0.316
16	5	4	50	104.58	0.087
17	5	4	50	112.41	0.277
18	5	4	50	113.62	0.076
19	5	4	50	105.37	0.250
20	5	4	50	100.97	1.054

Table 3: Experiments and recovery values for the elution of Cd(II)



Run	X_1 Flow rate (mL min^{-1})	X_2 Eluent Concentration (mol L^{-1})	X_3 Eluent volume (mL)	Recovery, %	Response
1	3	0.25	4	100.56	1.786
2	5	0.25	4	95.60	0.227
3	3	0.75	4	105.68	0.176
4	5	0.75	4	96.88	0.320
5	3	0.25	6	107.40	0.135
6	5	0.25	6	108.36	0.120
7	3	0.75	6	104.28	0.234
8	5	0.75	6	100.80	1.250
9	4	0.5	5	99.60	2.500
10	2.3	0.5	5	98.80	0.833
11	5.7	0.5	5	95.90	0.244
12	4	0.08	5	105.50	0.182
13	4	0.92	5	102.30	0.435
14	4	0.5	3.3	54.78	0.022
15	4	0.5	5	108.35	0.120
16	4	0.5	5	95.60	0.227
17	4	0.5	5	96.90	0.323
18	4	0.5	5	102.50	0.400
19	4	0.5	5	100.80	1.250
20	4	0.5	5	96.90	0.833

Table 4: Optimum preconcentration conditions for Cd(II) by GO–H_2P



Optimal conditions			
sorption		*elution*	
pH	2.9	Flow rate (mL.min^{-1})	4.1
Flow rate (mL.min^{-1})	4.3	Eluent Concentration (mol L^{-1})	0.6
Sample volume (mL)	55	Eluent volume (mL)	5.1

Table 5: Separation of Cd(II) from binary mixtures [a]

Diverse ion	Amounts taken(mg)	% Found	%Recovery of Pb^{2+} ion
Na^+	92.4	1.15(2.4)[b]	98.7(1.8)
K^+	92.5	1.32(2.3)	98.5(2.9)
Mg^{2+}	14.5	0.7(1.2)	98.9(1.8)
Ca^{2+}	26.3	2.25(3.0)	98.5(1.6)
Sr^{2+}	2.45	2.85(2.5)	98.4(2.0)
Ba^{2+}	2.66	3.16(2.1)	98.3(2.3)
Mn^{2+}	2.66	1.75(2.2)	97.3(2.8)
Co^{2+}	2.16	1.4(2.3)	99.1(2.9)
Ni^{2+}	1.65	2.0(2.4)	98.5(2.6)
Zn^{2+}	2.78	1.97(2.1)	98.4(2.2)
Cr^{3+}	2.55	1.92.0)	98.2(2.8)
Pb^{2+}	0.54	2.7(1.9)	97(2.7)
Hg^{2+}	0.44	2.81(2.1)	97.7(2.8)
Ag^+	2.63	3.45(2.9)	96.6(2.9)
Cr^{3+}	1.73	2.92(2.30	97.3(2.4)
UO^{2+}	2.84	2.8(2.1)	98.3(2.7)

[a] *Initial samples contained 10μg Pb^{2+} and different amounts of various ions in 100 mL water(0.1 M acetate ion).*
[b] *Values in parentheses are RSDs based on five individual replicate analysis.*

Table 6: Analysis of standard reference material

	Certfied Value	Found value	Recovery, %
CRM (TMDA-53.3)	118.0 ±9.3	127.6±11.7	108.1

Table 7: Recovery of Cd(II) added to 1000mL of different water samples (contaning 0.1Macetate at pH= 5.0)

Sample	Pb^{2+} added (μg)	Pb^{2+}determined(ng.mL^{-1})	ICP-AES
Tap water	0.0	1.74(1.4)[a]	ND
	10.0	11.98(3.2)	11.7
Snow water	0.0	4.45(2.4)	ND
	10.0	14.97(2.0)	14.7
Rain water	0.0	2.65(2.3)	ND
	10.0	12.75(2.4)	12.3
Sea Water	0.0	12.64(2.3)	12.5
	10.0	22.93(2.0)	23.1

[a] *Values in parentheses are %RSDs based on five individual replicate analysis*
[b] *Not detected*

Table 8: Comparison with other solid phase adsorbents

References	Eluent	Preconcentration factor	Method	Chelating agent/solid phase adsorbent
Pawliszyn	7 mol L^{-1}HCl	200	FAAS	Dithizone/microcrystalline naphthalene
Akama	0.1 mol L^{-1} HNO3	50	Atomic absorption spec-trophotometry	β-Naphthol/polyurethane foam
Alfassi	10 mol L^{-1} HCl	200	FAAS	Dithizone/silica gel
Hagen	Tetraphenyl-borate	80	Anodic stripping voltammetry	HgI_4^{2-}-Aliquat-336/naphthalene
Moghimi 2013	H_2SO_4 –H_2O_2 mixture	40	ICP-AES	DuoliteGT-73 resin
Huang	Water	5	FAAS	Dithioacetal/SiO_2
Krueger	1 mol L^{-1}HBr	50	FAAS	Hexathia18 crown-6 tetraone/Empore disk
Shamsipur	1 mol L^{-1}HBr	100	FAAS	1,5-Diphenylcarbazone/SDS coated alumina
Cuculic	HNO_3	–	ICP-AES	1,5-Bis(2-pyridyl)-3-sulfophenylmethylene) thiocarbonohydrazide/Dowex anion exchange resin
Gupta	6 mol L^{-1}HCl	50	FAAS	4-(2-Pyridyl azo) resorcinol/nano-sized SiO2
Choi	2 mol L^{-1} HNO_3 in acetone	300	FAAS	2-Mercaptobenzoxazole/chromosorb
Present work	HNO_3	200	FAAS	Graphene oxide with covalently linked porphyrin (GO–H_2P)

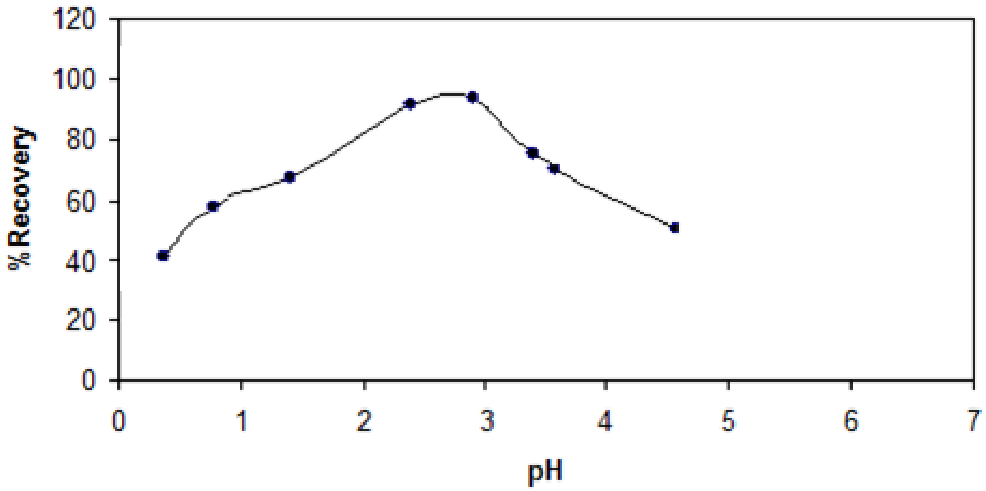


Figure 4: Influence of sample pH and dissolving solvent of GO–H_2P on the percentage recovery of Cd(II)

Validation and Application of the Improved Method

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

Real Sample Analysis

To assess the applicability of the method to real samples, it was applied to the extraction and determination of Cd(II) from different water samples. Tap water (Tehran, taken after 10 min operation of the tap), rain water (Tehran, 2015), Snow water (Varamin, 2015) 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 Cd(II) ions can be quantitatively recovered from the water samples used. As is seen, the recovered Cd(II) ion reveals that the results are quite reliable and are in satisfactory agreement with those obtained by ICPAES (Table 7).

Conclusion

In the present study, a new sorbent is prepared by using nano Graphene oxide with covalently linked porphyrin (GO–H_2P) and for preconcentration of Cd(II) from natural water samples. The modified nano Graphene oxide with covalently linked porphyrin (GO–H_2P) was prepared easily and sorbed Cd(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–H_2P 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 Pbpreconcentration with GO–H_2P is comparable to, or better than, some of the previously reported nano Graphene oxide with covalently linked porphyrin (GO–H_2P) based modified adsorbents. Finally, the proposed method can be suggested as simple, sensitive, accurate and repeatable method for determination of Cd(II) after preconcentration. This new enrichment procedure can also be applied to some other metal ions.

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