Int. J. Bio-Inorg. Hybr. Nanomater., 11(2): 79-88, Summer 2022

Solid Phase Extraction of trace Cd(II) ions in water samples by Modified nano graphene oxide nano-plate

F. Haji Karimi[1], N. Tajodini[2*]

[1] Department of Organic Chemistry, Faculty of Pharmaceutical Chemistry,
Tehran Medical sciences, Islamic Azad university, Tehran, Iran
[2] Department of Chemistry, Islamic Azad University, Varamin(Pishva) Branch, Varamin, Iran

Received: 11 November 2021; Accepted: 13 January 2022

ABSTRACT: The present method is a Flame atomic absorption spectrophotometric (FAAS) method for determining of trace Cd(II) after adsorption by modified by 2-aminopyridine/graphene oxide nano-plates. modified by 2-aminopyridine/graphene oxide nano-plates has a good capacity to retain Cd(II), but raw and purified as graphene oxide nano-plates does not absorb Cd(II) ions. Graphite Flame Atomic Absorption Spectroscopy (FAAS) was used to determine Cd(II). The effects of solution pH, washing conditions on the trace preconcentration of Cd(II) were studied and the effect of interfering ions was also investigated. The preconcentration factor of 100 was obtained. The method was successfully used to recover Cd(II) in various water samples. modified by 2-aminopyridine/graphene oxide nano-plates in this study has a high potential to be used as an excellent adsorbent in a separation method such as dispersive solid phase extraction (DSPE). The limit of detection of the proposed method is 20 μg l^{-1}. The maximum sorption capacity of the sorbent under the optimum conditions has been found to be 5mg of Cd(II) per gram of sorbent. The relative standard deviation under the optimum conditions was 2.2% (n= 10).

Keywords: *atomic absorption spectrometry(FAAS), adsorption, Cd(II)ion, Graphene oxide nano-plates, Preconcentration of heavy metals, SPE.*

INTRODUCTION

In recent years, environmental pollution by heavy metals has received considerable attention. Soluble cadmium ion and its compounds are toxic even in very small amounts and are stored in organs and the environment. Inhalation of cadmium dust quickly causes respiratory and kidney problems that can be fatal (often from kidney failure). Eating any significant amount of cadmium causes rapid poisoning of the liver and kidneys [1]. Dispersive solid phase extraction methods are possible for separation and preconcentration and determinate by flame atomic absorption spectroscopy (FAAS) [2]. Although, the determination of trace metal ions in natural waters is difficult due to various factors, particularly their low concentrations and matrices effects. Pre-concentration and separation can solve these problems and can lead to a higher confidence level and easy determination of the trace elements. Several procedures have been developed for the separation and preconcentration of contaminants from environmental matrices,such

---

(*) Corresponding Author - e-mail: nilofar_tajdini@yahoo.com as: liquid–liquid extraction (LLE) [3–8], co-precipitation [9–11], solid phase extraction (SPE) [12–20]. Although, disadvantages such as significant chemical additives, solvent losses, complex equipment, large secondary wastes, unsatisfactory enrichment factors and high time consumption, limit the application of these techniques. These problems could be addressed by the development of modular and compact processes that provide adequate separation and preconcentration without complex processes. The solvent microextraction technique effectively overcomes these difficulties by reducing the amount of organic solvent as well as allowing sample extraction and preconcentration to be done in a single step. The technique is faster and simpler than conventional methods. It is also inexpensive, sensitive and effective for the removal of interfering matrices. Solvent microextraction is a form of solvent extraction with phase ratio values higher than 100 [1]. Compared with the conventional solvent extraction, microextraction may provide poorer analyte recovery, instead the concentration in the organic phase greatly enhances. In addition, the amount of the used organic solvent is highly reduced and only one step of manipulation is necessary, therefore, problems of contamination and loss of analytes vanishes. Similarly, a solvent extraction study intended for separative recovery of cadmium, nickel, zinc and copper from smelting wastewater first extracted all the mentioned metals and subsequently selectivelystripped one metal at a time using progressively more acidic stripping solution after each metal removal [21-33]. Consequently, in the current investigation, the researchers focused on the first application of 2-aminopyridine/graphene oxide nano-plates as a novel adsorbent for dispersive solid-phase and extraction of Cd(II) wastewater samples before the flame atomic absorption spectrometry.

EXPERIMENTAL

Instrumentation

The determination of Cd(II) by PG-990 flame atomic absorption spectrometer is equipped with HI-HCl which was done according to the recommendations of the manufacturers. Accordingly, the pH measurements were used by Sartorius model PB-11.

Materials

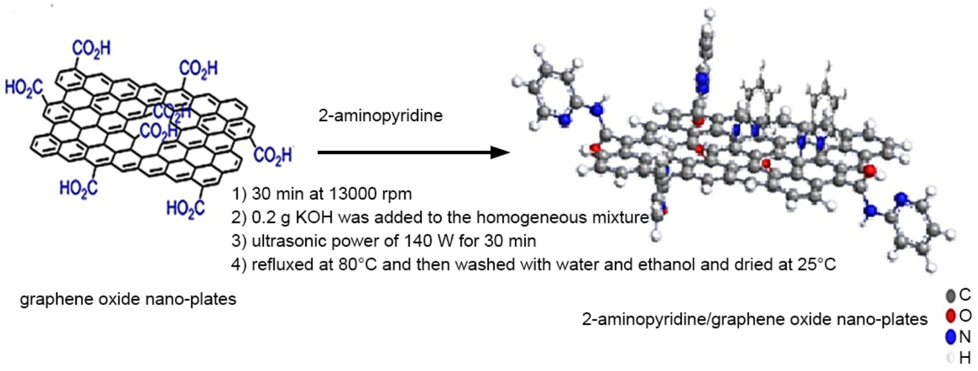
In the current investigation, the following materials have been applied for the experiments; graphene oxide nano-plates, hexahydrate Cd(II), thio-semi-carbazide ligand, buffer, and nitric acid. Additionally, ethylenediamine, thio-semi-carbazide ligand (CH_5N_3S) was prepared from Darmstadt, Germany of Merck.

Synthesis GrO

To prepare GrO, a certain amount of graphite oxide powder (0.1 g) was placed in 100 mL of water and ethanol solution (50/50%, v/v) under ultrasonic power of 140 W for 2 h. The resulted powder was dried in a vacuum desiccator [31].

GrO functionalized with 2-aminopyridine

The 0.1 g of GrO powder was poured in 200 mL of deionized water, then 0.2 g of 2Ap was poured and the mixture was placed in a homogenizer for 30 min at 13000 rpm. Then, the 0.2 g KOH was added to the homogeneous mixture and was subjected to ultrasonic power of 140 W for 30 min. The precipitate was re-



1) 30 min at 13000 rpm
2) 0.2 g KOH was added to the homogeneous mixture
3) ultrasonic power of 140 W for 30 min
4) refluxed at 80°C and then washed with water and ethanol and dried at 25°C

Fig. 1. Preparation of graphene oxide functionalized with 2-aminopyridine.

fluxed at 80 °C and then washed with water and ethanol and dried at 25°C (Fig. 1) [32].

The initial experiment of Cd(II) extraction for determining the suitable adsorbent

The procedure for extraction and recovery of Cd(II) ions by 2-aminopyridine/graphene oxide nano-plates is as follows; in the first step, 0.20 g of thiosemicarbazone ligand and 0.30 g of 2-aminopyridine/graphene oxide nano-plates and were dissolved in the little amount of acetone, and then it dried. Four 50-mL ballons were adopted, and then 0.050 g of 2-aminopyridine/graphene oxide nano-plates was poured into one of the balloons. Thereupon, a 1 ml buffer solution with a pH of 7.0 was added to balloons and a 2.0 ppm solution was prepared with an analyte. Four solutions were shaken at 25°C for 20 min, then these solutions for 15 min were centrifuged and the supernatant injected into an atomic absorption apparatus.

The effect of adsorbent amount for Cd(II) extraction

Seven 2.0 ppm solutions with 50 mL of Cd(II) were provided and poured into seven flasks. Seven solutions were adjusted at pH=7.0 (optimum pH) and different amounts of the adsorbent (0.005, 0.01, 0.03, 0.05, 0.07, 0.12, and 0.15) added to flasks. The mixtures were shaken for 20 min, and then the mixtures were centrifuged and the top solution of the examine tube injected in flame atomic absorption spectrophotometry.

Application on real samples

Once the extraction method was performed by the adsorbent, optimal conditions were achieved for it, and Multiple real aqueous samples were investigated. The real samples were as follows; well and drinking water in Pishva Town were collected with temperatures of 20 and 22°C, pH=7.1, 7.3 in 23.8.95 at 9:45, 10:00, respectively. Finally, a fish farming sample was collected at, pH=7.20 in 23.8.95 at 11:20. First, these suitable bottles were provided for the sampling of samples. The bottles were washed first with ordinary and distilled water. The bottles dried completely, and the 'suitable' label was attached to each bottle. To collecting of water samples, the used containers sample dried and cleaned and they had already been washed. For the analysis of the samples in the first stage, colloidal and suspended particles were removed. To this aim, the water samples passed through 0.22 μm filters. Next, the volume of 100 mL of samples was poured into the sample container. The pH of samples was adjusted at 10 and then, graphene oxide nano-plates and ligand were added to samples. They stirred for 20 min and the mixture was then centrifuged. Then, they were washed with HNO_3 0.1 M and were shaken again for 20 min. Finally, following the centrifugation of the mixture, absorption of Cd(II) ion was identified from the filtered solution by flame atomic absorption spectrophotometry. In the first step, the sample itself was injected into the apparatus without any Cd(II) ion, wherein water samples, the device displayed no absorption. To identify certain amounts of Cd(II) of the samples, the method of standard elevation was used. This stage was accomplished like the first step, the only discrepancy was that 0.5 mL of 200 ppm solution with Cd(II) added to the water samples. Finally, the absorption of Cd(II) ion was identified from the filtered solution by flame atomic absorption spectrophotometry.

RESULT AND DISCUSSION

This section deals with the results of the research experiments. The results achieved in the experimental chapter, calibration curve, and the factors influencing the extraction (e.g. pH, temperature effect, time, etc.) of Cd(II) ion by the 2-aminopyridine/graphene oxide nano-plates are discussed which are followed in the presentation of scientific justification and overall conclusion of the study.

Investigation of the influential factors on Cd(II) extraction

Study the effect of pH on Cd(II) extraction

The results of this study are provided in Fig. 2. As the results in Fig. 2 indicate, at pH=7.0, Cd(II) adsorption was maximized, while at lowest and highest pHs, the extent of adsorption declines, inferring that at pH<7.0 adsorptions of Cd(II) ions cannot occur completely. As revealed in Fig. 2, to determine the amount of 2-aminopyridine/graphene oxide nano-plates required for effective removal of Cd(II), different amounts of the

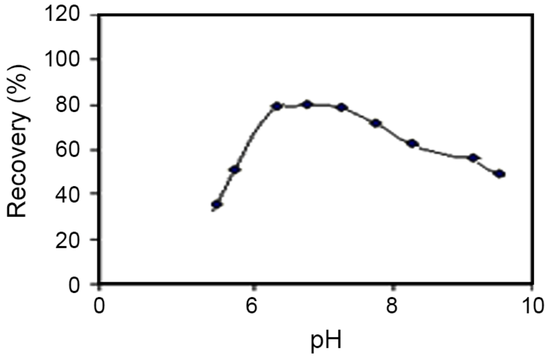


Fig. 2. The effect of pH in the Cd(II) adsorption.

2-aminopyridine/graphene oxide nano-plates (50 mg) for modification of 2-aminopyridine/graphene oxide nano-plates with fixes amount (3 mg) and its effect for the removal of Cd(II) from 20 mL solutions of Cd(II) (50 µg/L) were investigated.

Investigation of the effect of time on Cd(II) extraction

Based on the results, the extent of absorption increases, and the Cd(II) ions present in the solution find more chance to be adsorbed in the adsorbent's sites. Therefore, the quantitative extraction of Cd(II) ion is possible for a period of longer than 20 min, and within durations longer than 20 min and more, the reaction happens completely.

Survey of the effect of type of various desorption solvent for recovery of Cd(II)

Based on the results (Table 1), KOH cannot be used as appropriate desorption and these bases do not possess a complete detergence power. Therefore, mineral acids with determined concentrations, H_2SO_4, and HNO_3 were applied. As shown in Table 1, the results of this table offer that all acids contain a good detergence power for Cd(II), but the recovery percentage of HNO_3 is higher than that of other acids. In an acidic environment, the possible deposits dissolved and recovery of these ions increased. However, the results obtained from nitric acid were better than H_2SO_4, in that 0.10 M of solution washed 89.29% of the Cd(II) ion adsorbent. So, for the rest of the experiments, nitric acid 0.10 M was used as the desorption solution.

Table 1. Selection of the appropriate desorption for recovery of Cd(II)

Solvent	Recovery (%)
HNO_3 0.1M	89.29(2.2)[a]
HNO_3 1M	86.39(2.2)
HNO_3 3M	65.75(2.7)
H_2SO_4 0.1M	56.68(2.8)
H_2SO_4 1M	60.80(2.7)
KOH 0.1M	35.96(2.6)

a) Measurement RSD after three replications

Table 2. The optimum volume of the desorption solvent

Solvent volume	Recovery (%)
2mL	35.20(2.4)[a]
5 ml	67.20(2.5)
7ml	90.60(2.7)
9 ml	90.69(2.4)
10 ml	89.08(2.1)
14 ml	89.23(2.8)

a) Measurement RSD following three replications

Survey of optimization of the volume effect of desorption solvent for Cd(II) recovery

After the investigation and choice of optimal desorption, the volume of solvent was investigated, with the results which are shown in Table 2. The volume of 7.0 mL for HNO_3 was selected as the optimal volume for washing.

Investigation the effect of breakthrough volume

Following the optimization of the pH of the desorption solvent and sample solution, etc., to elute the Cd(II)in the adsorbents, the maximum volume of the aqueous solution containing Cd(II) should be measured. If the volume of the test solution to be less than the breakthrough volume, and passaging of that volume, all analytes are kept in the solid phase. The results in (Table 3) verify that up to 250 mL of ions are adsorbed by the nano adsorbents and if the sample volume is greater than this value, some of the Cd(II) is not kept on the adsorbent and pass over the adsorbent with no inhibition. Also with definition by the concept of breakthrough volume, it can be reported that the break-

Table 3. investigations of the effect of solution volume in the sample

V(ml)	Recovery (%)
50	88.2(2.5) [a]
100	87.94(2.5)
250	86.98(2.4)
500	87.75(2.3)
700	86.4(2.4)
800	60.9(2.6)
1000	49.9(2.9)

a) Measurement RSD following three replications

through volume in the current study is 700 mL and if the sample solution volumes which includes Cd(II) is over 700 mL, adsorption does not occur completely and hence if 250 mL of sample volume is passed over the adsorbent and then with 10 ml of the desorption solvent washed, the concentration factor could not be achieved as 30. This concept that the concentration of Cd(II) in 10 mL of desorption solvent which was passed over the adsorbent grows by 100 times. Based on the related results (Table 3), the breakthrough volume calculations are as follows:

Concentration factor = breakthrough volume/the desorption solvent volume= 700/7=100

Determination of the blank standard deviation (S_b)

The accuracy or replicability of any method is the main factor to recognize its validity and reliability. To inquire about the method's replicability, the results data of the study of four blank solutions (deionized water). Based on the results achieved, the blank standard deviation was obtained as follows; S_b=0.0006

Determination of the accuracy and RSD% of the method

This parameter was used to investigate the accuracy and proximity of the examined data. As shown in 2.2% standard deviation has been calculated for three tests and the relative standard deviation (RSD) achieved for three replications.

The linear range and a calibration curve of the method

To assess the linear range in the analysis method, a calibration curve should be plotted. This curve is not linear across all concentrations and different factors cause the calibration curve to the situation in the linear range and follow from Beyer Law. the calibration curve of the method is as conform and the line equation is y=0.091x+0.023 and R2=0.99924.

Study of the effect of disturbances on the measurement of Cd(II)

A disturbing ion is an ion that causes a certain variation of over ±5% in the adsorption and recovery of Cd(II) To study the effect of disturbance of other ions on Cd(II) extraction, a certain quantity of interfering factors added to the initial solution, and the experiment was performed at breakthrough volume. Absorption of the recovered solution is analyzed with flame atomic absorption and then compared versus the solution absorption resulting from the sample recovery

Table 4. The effect of interfering ions on the recovery of Cd(II)

Ions	Added Value(ppm)	Recovery Percentage Cd(II)
Na^+	100	88.95(2.5) [a]
Zn^{2+}	3.0	89.36(2.4)
K^+	100	89.86(2.4)
Mg^{2+}	200	88.65(2.7)
Cu^{2+}	4.0	89.70(2.8)
Cl^-	500	88.78(2.5)
NO_3^-	320	89.20(2.4)
SO_4^{2-}	200	89.90(2.5)

a) Measurement RSD after three replications

Table 5. Determination of Cd(II) in the real sample

Recovery	R.S.D.% (n =5)	This method (µg.g $^{-1}$)*	Reference method (µg.l $^{-1}$)*	Samples
89.6	2.6	48	50	Tap water
90.2	2.7	545	538	Pure water
89.0	2.3	349	350	Industrial wastewater

*, Average of five determinations.

which lacks the interfering ion. As can be shown in Table 4, in the presence of external ions, Cd(II) recovery occurred with ±5% variations and the external ions had no particular effects on the analysis and cause no disturbance.

Determining the method's limit of detection

The lowest Cd(II) concentration or weight in a sample that could be determined with a certain confidence level is called the limit of detection (LOD), which is defined as follows. The LOD of a method is a concentration of an analysis sample where the device response to concentration (which is significantly different from the response of the control sample) is defined as follows; the limit of detection is the lowest amount of Cd(II), where the presented method can detect it. Based on the presented definition, LOD can be calculated by the following relation;

$$\mathrm{LOD} = \frac{3S_b}{m} \quad (1)$$

Where S_b and m are the standard deviations of the blank signal and the slope of the calibration curve, respectively. Based on the experimented, Sb=0.0006 and the slope of the calibration curve is 0.091.
Therefore, LOD can be calculated at 20.0 ppb.

Investigation of the obtained results on real sample

The proposed method has been successfully applied to the determination of Cd(II) in three real drinking water samples (tap water of tehran, pure water and industrial wastewater sample of Charmshar Varamin. The results were shown in Table 5, together with results of a recovery test by added known amounts of silver in water sample. The results of this analysis are shown in Table 5, the level of Cd(II) ions was measured across different water and biological samples at 250 mL. As can be seen, in the water samples, in the Tap water sample of Tehran, on 20 January 2023, and industrial wastewater sample of Charmshar Varamin on 20 January 2023, there is a larger amount of Cd(II) than in the experimented water samples. Although, in other samples, there is less Cd(II) ions. Based on this, the performance and power of preconcentration and Cd(II) ions measurement could be deduced.

A comparison between the current method and other methods

A comparison of this method with other methods verified that the current method is more accurate, easiest, and faster as it had smaller relative standard deviation values in comparison with other methods [36-52]. The current method is one of the foremost systems for determining the very trace amounts of heavy metal ions including Cd(II) in aqueous samples. Another point in the usage of graphene oxide nano-plates adsorbent is that instead of using the proposed ligand, one can put other ligands on the adsorbent which to adsorb mineral ions, thereby measuring trace amounts of metal ions. A wide variety of ligands can be used given their properties, which act selective towards one or several ions and applying this set, preconcentration, and determination of cations can be carried out. Using flame atomic absorption and solid drop microextraction, single-drop liquid-liquid extraction, and homogeneous liquid-liquid extraction with other devices, one can determine trace amounts of Cd(II) by this adsorbent and achieve a smaller limit of detection value.

CONCLUSION

In comparison with other procedures reported for measurement of Cd(II), this method has considerable advantages that are easy and inexpensive and can be applied quickly for environmental aqueous samples. Furthermore, it minimizes the utilization of organic, toxic, and costly solvents. Moreover, the design and development of this procedure for separation, measurement, and preconcentration of Cd(II) are essential considering its importance in various industries and the little concentration of Cd(II) ion in most samples. Therefore, this research aims to present an effective, selective, cost-effective, and simple method for measurement of the level of Cd(II) across different environmental aqueous samples (in this research, the limit of detection, the value of breakthrough volume, and RSD has been obtained). This research indicated that the measurement of Cd(II) occurs at an appropriate level without the interference of any other interfering factor and thus the current method can be applied easily in the measurement of the quantity of Cd(II) in aqueous samples.

ACKNOWLEDGMENTS

We gratefully acknowledge the financial of the Department of Chemistry, Faculty of Pharmaceutical Chemistry, Tehran Medical Sciences Islamic Azad University for financial support.

REFRENCES

[1] Magnetic susceptibility of the elements and inorganic compounds, in Handbook of Chemistry and Physics 81st edition, CRC press.

[2] Moghimi, A., Qomi, M., Yari, M., Abniki, M. (2019). Solid phase extraction of Hg(Π) in water samples by nano-Fe. Int. J. Bio-Inorg. Hybr. Nanomater., 8(4), 163-172.

[3] Bulte, J.W.M. (2006). Intracellular endosomal magnetic labeling of cells, Methods Mol. Med., 124, 419-439.

[4] Bruening, M.L., Mitchell, D.M., Bradshaw, J.S., Izatt, R.M., Bruening, R.L. (1991). Removal of cesium from alkaline waste solution: Part VI – Column ion exchange study. Anal. Chem., 63, 21-27.

[5] Bulte, J.W.M., Douglas, T., Witwer, B., et al. (2001). Magnetodendrimers allow endosomal magnetic labeling and in vivo tracking of stem cells. Nat. Biotechnol., 19, 1141-1147.

[6] Campderros, M.E., Acosta, A., Marchese, J. (1998). Selective separation of copper with Lix 864 in a hollow fiber module. Talanta, 47, 19-23.

[7] Moghimi, A., Abniki, M. (2021a). Dispersive Solid-Phase Extraction for Bromocresol Green Removal with β-Cyclodextrin Functionalized Magnetic Nanotubes. Russ. J. Phys. Chem. B, 15(1), S130-S139.

[8] Moghimi, A., Qomi, M., Yari, M., Abniki, M. (2019). Solid phase extraction of Hg(Π) in water samples by nano-Fe. Int. J. Bio-Inorg. Hybr. Nanomater., 8(4), 163-172.

[9] Pourshamsi, T., Amri, F., Abniki, M. (2021). A comprehensive review on application of the syringe in liquid-and solid-phase microextraction methods. J. Iran Chem. Soc., 18(2), 245-264.

[10] Arpadjan, S., Vuchkova, L., Kostadinova, E. (1997). Study of the adsorption behavior of heavy metal ions on nanometer-size titanium dioxide with ICP-AES. Analyst, 122, 243-250.

[11] Moghimi, A., Abniki, M. (2022). Removal and measurement of bromocresol purple dye in aqueous samples by β-cyclodextrin-modified magnetic carbon nanotube with dispersive solid-phase extraction technique. J. Color Sci.Technol., 15(4), 301-315.

[12] Boll, I., Kramer, R., Brunner, J., Mokhir, A. (2005). Oligonucleotide-Templated Reactions for Sensing Nucleic Acids. J. Am. Chem. Soc., 27, 7849-7855.

[13] Brunner, J., Mokhir, A., Kramer, R. (2003). Copper(II)-Quenched Oligonucleotide Probes for Fluorescent DNA Sensing. J. Am. Chem. Soc. 125, 12410-12415.

[14] Bruening, M.L., Mitchell, D.M., Bradshaw, J.S., Izatt, R.M., Bruening, R.L. (1991). Removal of cesium from alkaline waste solution: Part II – Column ion exchange study), Anal. Chem. 63 21-27.

[15] Bulte, J.W.M., (2006), In tracellularendosomal magnetic labeling of cells ,Methods Mol. Med. 124:419–439.

[16] Campderros, M.E., Acosta, A., Marchese, J. (1998). Selective separation of copper with Lix 864 in a hollow fiber module. Talanta, 47, 19-23.

[17] Caroli, C., Alimanti, A., Petrucci, F., Horvath, Z. (1991). Selective pre-concentration and solid phase extraction of mercury(II) from natural water by silica gel-loaded dithizone phases. Anal. Chim. Acta, 248, 241-247.

[18] Choi, Y.S., Choi, H.S. (2003). Studies on Solvent Sublation of Trace Heavy Metals by Continuous Flow System as Ternary Complexes of 1,10-Phenanthroline and Thiocyanate Ion. Bull. Korean Chem. Soc., 24, 222-228.

[19] Cuculic, V., Mlakar, M., Branica, M. (1997). Synergetic adsorption of copper(II) mixed ligand complexes onto the SEP-PAK Cl8 column. Anal. Chim. Acta, 339,181-189.

[20] Salehi, N., Moghimi, A., Shahbazi, H. (2021). Magnetic nanobiosorbent (MG-Chi/Fe3O4) for dispersive solid-phase extraction of Cu(II), Pb(II), and Cd(II) followed by flame atomic absorption spectrometry determination, IET. Nanobiotechnol., 15, 575-584.

[21] Salehi, N., Moghimi, A., Shahbazi, H. (2022). Preparation of cross-linked magnetic chitosan with methionine-glutaraldehyde for removal of heavy metals from aqueous solutions. Int. J. Env. Anal. Chem., 102, 2305-2321.

[22] Arvand, M.P., Moghimi, A., Salehi, N. (2023). A novel removal of Ni(II) ions from water solutions using dispersive solid-phase extraction method with nano Fe3O4/chitosan-acrylamide hydrogel. https://doi.org/10.21203/rs.3.rs-2439474/v1

[23] Tajodini, N., Moghimi, A., Karimnezhad, K. (2020). Separation of levodopa using Nanotubes Carbon modified Methyl Amine in biological samples and determination by UV-Vis Spectrophotometry. J. Adv. Pharm. Edu. Res., 10(S4), 153-163.

[24] Grote, M., Kettrup, A. (1985). Liquid-liquid extraction of noble metals by formazans: Analytical Applications of Silver Extraction by ortho-Substituted Formazans. Anal. Chim. Acta, 175, 239-244.

[25] Hummers, W.S., Offeman, RE. (1958). Preparation of graphitic oxide. J. Am. Chem. Soc., 80, 1339-1344.

[26] Krueger, C.J., Fild, J.A. (1995). Method for the analysis of triadimefon and ethofumesate from dislodgeable foliar residues on turfgrass by solid-phase extraction and in-Vial elution. Anal. Chem., 67, 3363-3369.

[27] Kvitek, R.J., Evans, J.F., Carr, P.W. (1982). Denaturation of purple membranes at the air/water interface studied by SEM. Anal. Chim. Acta, 144, 93-98.

[28] Leyden, D.E., Luttrell, G.H., Nonidez, W.K., Werho, D.B. (1976). Adsorption of Co(II) and Cu(II) on silica gel surface modified with pyridinium ion from acetone and ethanol solutions. Anal. Chem., 48, 67-72.

[29] Moghimi, A., Abniki, M., Khalaj, M., Qomi, M. (2021). Construction of modified nanotube carbon carboxyl by new method and application in dispersive solid phase extraction for preconcentration of Ni(II). Revue Roumaine de Chimie, 66(6), 493-507.

[30] Moghimi, A., AbnikI, M. (2021). The Dispersive Solid-Phase Extraction of Fluoxetine Drug from Biological Samples by the Amine-Functionalized Carbon Nanotubes with HPLC Method. Chem. Methodol., 5(3), 250-258

[31] Liu, J., Wang, Y., Xu S., Sun, D.D. (2010). Synthesis of graphene soluble in organic solvents by simultaneous ether-functionalization with octadecane groups and reduction. Mater. Lett., 64, 2236-2239.

[32] Salehi, N., Moghimi, A., Shahbazi, H. (2021). Magnetic nanobiosorbent (MG-Chi/Fe_3O_4) for dispersive solid-phase extraction of Cu(II), Pb(II), and Cd(II) followed by flame atomic absorption spectrometry determination. IET Nanobiotechnol., 15, 575-584.

[33] Mahmoud, M.E. (1997). Silica-immobilized formylsalicylic acid as a selective phase for the extraction of Iron(III). Talanta, 44, 15-21.

[34] Mahmoud, M.E., Soliman, E.M. (1997). Study of the selective extraction of Iron(III) by silica-immobilized 5-formyl-3-arylazo-salicylic acid derivatives. Talanta, 44, 1063-1071.

[35] Moghimi, A., Abniki, M. (2021). Preconcentration and Separation of Ultra-Trace Cu (II) with

Disks of Octadecyl Silica Membrane Modified Nano-Fe3O4-Encapsulated-Dioctyl Phthalate and Linked-Diethylenetriamine. Adv. J. Chem. Sec A, 4(2), 78-86.

[36] Mahmoud, M.E. (1999). Selective solid phase extraction of mercury(II) by silica gel-immobilized-dithiocarbamate derivatives. Anal. Chim. Acta, 398, 297-302.

[37] Motallebi, R., Moghimi, A., Shahbazi, H., Faraji, H. (2022). Fabrication of superparamagnetic adsorbent based on layered double hydroxide as effective nanoadsorbent for removal of Sb(III) from water samples. IET Nanobiotechnol., 16(2), 33-48.

[38] Moghimi, A., Tajodini, N., Karimnezhad, K. (2021). Alternative Method of Extraction of ultra-trace Co(II) with disks of octadecyl silica membrane modified nano-Fe3O4-encapsulated-dioctyl phthalate and linked-diethylenetriamine. Eur. J. Mol. Clin. Med., 8(1), 2080-2088.

[39] Moghimi, A., Ghiasi, R., Abedini, A.R., Ghammamy, S. (2009). Solid phase extraction of Cd(II) using mesoporous organosilicas and determination by FAAS. Afr. J. Pure Appl. Chem., 3(3), 051-059.

[40] Moghimi, A., Tajodini, N. (2010). Preconcentration of Copper(II) in Water Samples Using Polyurethane Foam/2-(6'-Ethyl-2'-benzothiazolylazo) chromotropic acid. Asian J. Chem., 22(5), 3325-3334.

[41] Abniki, M., Moghimi, A., Azizinejad, F. (2021). Fabrication of bionanocomposite based on LDH using biopolymer of gum arabic and chitosan-coating for sustained drug-release. J. Serb. Chem. Soc., 85(9), 1223-1235.

[42] Moghimi, A. (2007). Preconcentration and Determination of Trace Amounts of Heavy Metals in Water Samples Using Membrane Disk and Flame Atomic Absorption Spectrometry. Chinese J. Chem., 25(10), 640-645.

[43] Moghimi, A. (2008). Preconcentration of Copper(II) Using Mesoporous Organo-Silicas and Determination by Flame Atomic Absorption Spectrometry. J. Korean Chem. Soc., 52(2), 155-163.

[44] Abniki, M., Moghimi, A., Azizinejad, F. (2021). Synthesis of calcium-layered double hydroxide based nanohybrid for controlled release of an anti-inflammatory drug. J. Chinese Chem. Soc., 68(2), 343-352.

[45] Moghimi, A., Tehrani, M.S., Waqif Husain, S. (2006). Preconcentration and Determination of Copper(II) Using Octadecyl Silica Membrane Disks Modified by 1,5-Diphenylcarhazide and Flame Atomic Absorption Spectrometry. Mat. Sci. Res. India, 3(1a), 27-32.

[46] Moghimi, A., Abdouss, M. (2012). Preconcentration of Ni(II) from sample water by modified poly (ethylene terephthalate)-grafted-acrylic acid/ acryl amide fiber. Afr. J. Pure Appl. Chem., 6(8), 110-118.

[47] Moghimi, A. (2014). Separation and extraction of Co(II) using magnetic chitosan nanoparticles grafted with β-cyclodextrin and determination by FAAS, Russ. J. Phys. Chem. A, 88(12), 2157-2164.

[48] Moghimi, A., Yari, M. (2019). Review of procedures involving separation and Solid Phase Extraction for the determination of cadmium using spectrometric techniques, J. Chem. Rev., 1(1), 1-18.

[49] Nambiar, D.C., Patil, N.N., Shinde, V.M. (1998). Liquid-liquid extraction of mercury(II) with triphenylphosphine sulphide: Application to medicinal and environmental samples. Fresenius J. Anal. Chem., 360, 205-212.

[50] Narin, I., Soylak, M., Elic, L., Dogan, M. (2000). An Evaluation of Loading Rate of Dust, Pb, Cd, and Ni and Metals Mass Concentration in the Settled Surface Dust in Domestic Houses and Factors Affecting Them. Talanta, 52, 1041-1047.

[51] Shojai, M., Moghimi, A., Reza Asghari, R. (2015). Preconcentration of Pb(II) on Micro Crystalline Naphthalene Modified with Organic-Solution-Processable Functionalized-Nano Graphene, Elixir Appl. Chem., 82, 32605-32609.

[52] Amiri, S., Asghari, A., Vatanpour, V., Rajabi, M. (2021). Fabrication of chitosan-aminopropylsilane graphene oxide nanocomposite hydrogel embedded PES membrane for improved filtration performance and lead separation. J. Environ. Manage., 294, 112918.

AUTHOR (S) BIOSKETCHES

Fateme Haji Karimi, Department of Organic Chemistry, Faculty of Pharmaceutical Chemistry, Tehran Medical sciences, Islamic Azad university, Tehran, Iran

Nilofar Tajodini, Assistant Professor, Department of Chemistry, Islamic Azad University, Varamin(Pishva) Branch, Varamin, Iran, *Email: nilofar_tajdini@yahoo.com*