



AENSI Journals

Advances in Environmental Biology

ISSN-1995-0756 EISSN-1998-1066

Journal home page: <http://www.aensiweb.com/AEB/>

Silver Nanoparticles-improved Liquid Phase Microextraction Followed with Flame Atomic Absorption Spectrometry for Quantitative Analysis of Cadmium in Real Water Samples

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ARTICLE INFO

Article history:

Received 11 June 2014

Received in revised form 21 August 2014

Accepted 25 September 2014

Available online 5 October 2014

Keywords:

Silver nanoparticles, Cadmium, Chelating agent, real Water sample, flame atomic absorption spectrometer (FAAS)

ABSTRACT

In this research, a practical and environmentally friendly liquid phase microextraction based on the application of silver nanoparticles modified with (4-mercaptophenyliminomethyl)-2-methoxyphenol, and ionic liquid was followed with atomic absorption spectrometry for preconcentration and quantitative analysis of cadmium. In this sample pretreatment method, a mixture containing 1-hexyl-3-methylimidazolium hexafluorophosphate ([Hmim][PF₆]), ethanol, modified silver nanoparticles and chelating agent was rapidly added to the sample solution using a proper syringe. After this step, complex of Cd was extracted into the ionic liquid phase. In order to collect the target analyte at the bottom of the test tube, the sample solution was centrifuged. By using the silver nanoparticles coated with an organic compound, the performance of the microextraction method was improved. The collected enriched phase was diluted and centrifuged again. The supernatant of the enriched phase was introduced to flame atomic absorption spectrometer (FAAS) for quantitative analysis of cadmium. Main parameters affecting the output of the developed procedure were evaluated in details and optimized. In the present technique, a linear dynamic range of 4-60 µg L⁻¹, a limit of detection (LOD) of 0.9 µg L⁻¹ and a relative standard deviation (R.S.D.) of 3.1% were achieved. Finally, this combined methodology was applied for quantitative analysis of cadmium in different real water samples.

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To Cite This Article: Kourosh Motevalli, Zahra Yaghoubi, Fereshteh Amini, Silver Nanoparticles-improved Liquid Phase Microextraction Followed with Flame Atomic Absorption Spectrometry for Quantitative Analysis of Cadmium in Real Water Samples. *Adv. Environ. Biol.*, 8(11): 1103-1107, 2014.

INTRODUCTION

Heavy metals such as cadmium show toxic behaviors and they may cause many problems for human health. The amount of heavy metals in real samples including water samples should be controlled by accurate and precise methods, in order to ensure that the concentration of these elements have not negative effect on human health. World Health Organization (WHO) recommends that permissible levels of cadmium in drinking water samples are 50 µg L⁻¹.

In literature, some analytical procedures have been utilized for quantitative analysis of Cd including flame atomic absorption spectrometry (FAAS) [1], inductively coupled plasma-mass spectrometry (ICP-MS) [2], electrochemical methods [3] and spectrophotometric methods [4]. However, the selectivity and sensitivity of these methods suffer from many limitations and therefore the development of the robust techniques for trace determination of cadmium in real samples is one of the most important tasks of the chemists.

In the presented study, it was demonstrated that by using the silver nanoparticles coated with an organic compound, the performance of the extraction method was improved which was due to the proper hydrophobic behavior of modified nanoparticles [5-7]. Finally, the developed method was applied for quantitative analysis of Cd in some real water samples.

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2. Experimental:

2.1. Apparatus:

A flame atomic absorption spectrometer (Shimadzu AA-6300) equipped with cadmium hollow-cathode lamp was applied for the quantitative analysis of Cd. A 1000 μ L Hamilton syringe was applied for injection of the extraction solvent into the sample solution.

2.2. General procedure for synthesis of the modified silver nanoparticles:

In this procedure, 6 mL of ethanol and 200 mg of vanillin were added into a 20 mL flask. Afterwards, 1 drop of acetic acid and 200 mg of 4-aminothiophenol was added to the above solution and stirred for 6 h at 25 $^{\circ}$ C. The resulting product was washed by proper amount of ethanol and dried to obtain 4-mercaptophenyliminomethyl)-2-methoxyphenol. AgNO_3 was reduced by NaBH_4 (0.01M) as a reducer agent, in order to obtain nanoparticles of Ag. In this method, 1 mL of NaBH_4 was added dropwise to 200 mL of 0.3 mM AgNO_3 solution. The prepared silver particles in water media was transferred to the toluene solution which contains 1.5 mM (4-mercaptophenyliminomethyl)-2-methoxyphenol. After this step, the resulting solution was stirred for 7 h. By using this procedure the modified silver nanoparticles was transferred into the organic phase and after the separation of organic phase, it was washed with water.

2.3. Characterization of the nanoparticles:

The silver nanoparticles coated with 4-mercaptophenyliminomethyl)-2-methoxyphenol were studied and characterized by utilizing scanning electron microscopy (JSM-6701F SEM system) (Figure 1).

2.4. Silver nanoparticles-improved liquid phase microextraction:

In the silver nanoparticles-improved ionic liquid phase microextraction, the pH of 30 mL of the sample was fixed at pH 6 and transferred to the sample vessel. Then, 700 μ L of ethanol containing 80 mg of $[\text{Hmim}][\text{PF}_6]$, silver nanoparticles coated with (4-mercaptophenyliminomethyl)-2-methoxyphenol and chelating agent was injected into the sample solution. A cloudy condition was obtained and complex of cadmium was extracted into the IL-phase. The performance of the extraction procedure was improved due to the presence of the coated silver nanoparticles. The obtained aqueous solution was centrifuged for 8 min at 5000 rpm. The aqueous phase was removed and the IL-phase was diluted with ethanol and centrifuged again. Afterwards, the supernatant of the resulting enriched phase was introduced to flame atomic absorption spectrometer (FAAS) for quantitative analysis of cadmium.

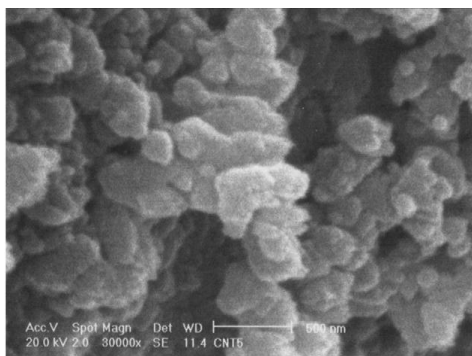


Fig. 1:

RESULTS AND DISCUSSION

3.1. Optimization of the kind of ionic liquid:

The kind of ionic liquid plays a significant role in the performance of the microextraction procedure. Density of Ionic liquid must be higher than water and it must show sufficient hydrophobicity. Ionic liquids containing imidazolium chains and PF_6^- and $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ ions show suitable hydrophobicity and their densities are high enough. Based on these facts, $[\text{Hmim}][\text{PF}_6]$ was selected as an optimum ionic liquid in all experiments.

3.2. Optimization of the kind of disperser solvent:

The disperser solvent must show a suitable miscibility in water media and ionic liquid phase, and have no toxicity effect. For this optimization step, some solvents such as acetone, ethanol, acetonitrile and methanol were tested. Based on the data obtained in this study, ethanol showed better performance in comparison with other solvents. Finally, because of proper sensitivity in using of ethanol and acceptable safety, this solvent was used as an optimum disperser solvent.

3.3. Influence of ionic liquid amount and volume of disperser solvent:

The amount of ionic liquid is one the most important factor in silver nanoparticles-improved liquid phase microextraction. This parameter evaluated in details, in order to obtain the best analytical signals. The amount of ionic liquid was tested in the range of 20-150 mg. As it is indicated in Fig. 2, by increasing the amount of ionic liquid, the sensitivity is increased and after a certain value, the analytical signal is decreased. Due to these data, 80 mg of IL was selected for the rest of the research.

In the next evaluation, the amount of disperser solvent was tested in the range of 200-800 μL . The results obtained in this study showed that better sensitivity is obtainable using 700 μL of ethanol. Finally, this value was selected for the rest of the research.

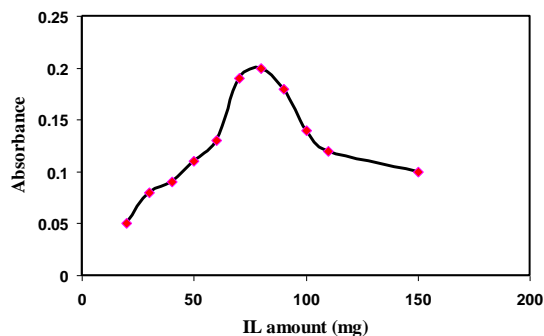


Fig. 2:

3.4. Optimization of pH:

In the presented work, after the reaction between Cd and chelating agent a hydrophobic complex is formed and extracted into the ionic liquid containing nanoparticles. Due to the formation of a hydrophobic complex, pH of the sample solution plays a main role in the extraction recovery. This parameter was studied in the range of 1-9 (Figure 3). Signals obtained in this range showed that the best analytical signal was obtained using a pH value of 6. For adjustment of pH, HCl and NaOH were applied.

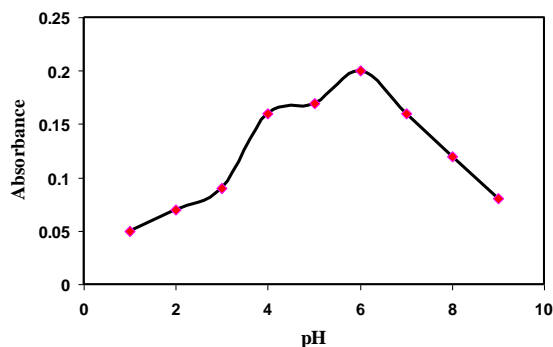


Fig. 3:

3.5. Optimization of Chelating agent concentration and kind of diluting solvent:

The Influence of various concentrations of Bis(2-methoxybenzaldehyde) ethylene diimine as the chelating agent on the absorbance was evaluated. The impact of this factor was tested in the range of 1×10^{-5} - 1×10^{-1} M. (Figure 4). Maximum absorbance and the best reproducibility was obtained at 1×10^{-3} , thus this value was selected as the optimal. The viscosity of the ionic liquid is high and it is not possible to inject it directly to FAAS, hence it should be diluted. Some solvents were tested as the diluting solvents, in order to obtain the best absorbance and safety. According the data obtained in this evaluation, ethanol showed all the criteria mentioned above.

3.6. Selectivity survey:

In the present test, the effect of other ions on the determination of Cd with a concentration of $30 \mu\text{g L}^{-1}$ was studied. The influence of some ions usually found in real water samples were evaluated. No ions was able to change the signals more that 5%.

3.7. Analysis of real samples:

The recommended method was applied for trace determination of Cd in real water samples including tap water, river water and sea water, in order to show the analytical application of the proposed method. The results

obtained in this study are shown in Table 1. These tests showed that the mean recoveries of Cd in water samples were within the range of 93.4-98%. These results revealed the proper applicability of the presented method for trace determination of Cd in real samples.

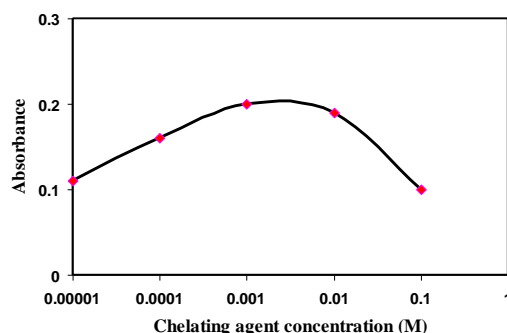


Fig. 4:

Table 1: Analysis of Cd in water samples using silver nanoparticles-improved ionic liquid phase microextraction-FAAS.

Samples	Added Value ($\mu\text{g L}^{-1}$)	Found Value ($\mu\text{g L}^{-1}$) ^a	Recovery (%)
	Cd	Cd	Cd
Tap water	-	ND ^b	-
	10	9.7 ± 0.4	97.0
	20	19.5 ± 0.7	97.5
River ^c water	-	4.8 ± 0.2	-
	10	14.3 ± 0.9	96.6
	20	25.0 ± 1.1	99.2
Sea water ^d	-	5.1 ± 0.3	-
	10	14.1 ± 0.8	93.4
	20	24.6 ± 1.2	98

^a Mean values \pm standard deviations (n=5).

^b Not detected.

^c Karaj river

^d Caspian sea

4. Conclusion:

In this research, a benign sample pretreatment method based on the application of silver nanoparticles modified with (4-mercaptophenyliminomethyl)-2-methoxyphenol, and ionic liquid was followed with FAAS for preconcentration and quantitation of Cd in water samples. By using the silver nanoparticles coated with an organic compound, the performance of the sample pretreatment method was improved. On the other hand, the interaction of the complex of Cd with ionic liquid was increased due to the presence of the nanoparticles in the extraction phase. Main parameters affecting the output of the developed procedure were evaluated in detail and optimized. In this microextraction method, no toxic solvent is applied, which increase its compatibility with green chemistry rules. The proposed methodology reveals many advantages such as simplicity, high speed, no usage of hazardous material, high extraction recovery and acceptable sensitivity and selectivity.

REFERENCES

- [1] Shemirani, F., S.D. Abkenar, S.S. Mirroshandel, A.A. Salavati-Niasari, R.R. Kozani, 2003. Colorimetric Determination of Benzocaine, Lignocaine and Procaine Hydrochlorides in Pure Form and in Pharmaceutical Formulations Using p-Benzoquinone. *Anal. Sci.*, 19: 1453-1456.
- [2] Sun, Y.C., C.Y. Lin, S.F. Wu, Y.T. Chung, 2006. Evaluation of on-line desalter-inductively coupled plasma-mass spectrometry system for determination of Cd, Cr(VI), and total cadmium concentrations in natural water and urine samples. *Spectrochim. Acta B* 61: 230-234.
- [3] Kiptoo, J.K., J.C. Ngila, G.M. Sawula, 2004. Speciation studies of nickel and cadmium in wastewater from an electroplating plant. *Talanta*, 64: 54-59.
- [4] Motevalli, K., M. Zeeb, 2011. Dispersive liquid-liquid microextraction using silver nanoparticles as electrostatic probes for preconcentration and quantitative analysis of terazosin. *Int. J. Nano Dimens*, 1: 187-201.
- [5] Zhou, Q., C. Ye, 2008. Ionic liquid for improved single-drop microextraction of aromatic amines in water samples. *Microchim. Acta.*, 162: 153-159.
- [6] Zhou, Q.X., H.H. Bai, G.H. Xie, J.P. Xiao, 2008. Temperature-controlled ionic liquid dispersive liquid phase micro-extraction. *J. Chromatogr. A* 1177: 43-49.

- [7] Saidi, A., M. Mirzaei, 2015. MCR of the quenching of the EEM of fluorescence of Aflatoxins (B1, G1) by Silver nanoparticles. *Int. J. Nano Dimens.*, 6: 31-38.