Synthesis and application of acrylamide-maleic anhydride copolymer for solid phase extraction

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Abstract. A new absorbent of acrylamide-maleic anhydride copolymer (PAMMA) for preconcentration of metal ions was synthesized. This PAMMA was applied for enrichment and determination of Al³⁺, Cu²⁺, Cd²⁺ and Pb²⁺ in table salt by ICP-OES. The maximum uptake capacities of PAMMA were 6.49, 5.84, 5.34 and 7.49 mg g⁻¹ for Al³⁺, Cu²⁺, Cd²⁺ and Pb²⁺, respectively. The limit of detection was 0.31, 0.26, 0.43, and 0.12 μg L⁻¹, and the RSD (relative standard deviations, n=6) was 1.5%, 3.7%, 3.0% and 2.6% for Al³⁺, Cu²⁺, Cd²⁺ and Pb²⁺, respectively. The presented method was used for simultaneous detecting of Al³⁺, Cu²⁺, Cd²⁺ and Pb²⁺ in table salt with the recoveries from 95.0% to 103%.

1. Introduction

The monitoring of trace metals in food and environmental samples has aroused considerable interest owing to their important roles in living organisms [1]. For example, copper is an essential micronutrient for living organisms, but it may be toxic at higher concentrations [2]. Aluminum is not an essential element for mammals, can accumulate in organism tissues and result in some diseases such as Alzheimer’s disease, neurotoxicity [3]. Lead and cadmium, even relatively low levels of concentration, are very toxic [4]. The metal elements of human body come mainly from foods, water, medicines and the use of metal cooking utensils.

Table salt is one of the most consumed products by humanity. Salt industry utilizes sea water or lake water in their process, since these waters often contain all sorts of elements, and table salt may include some of these elements. Hence, determination of very low levels of metal ions in table salt has become increasingly very important.

ICP-OES is widely applied in the detecting of metal ions due to attractive features such as multi-element detection capacity, wide linear range and low limits of detection. However, ICP-OES is not suitable for direct detecting of trace metals in salt samples, because the aspiration of the high salt solutions in the plasma can cause blockage of the nebulizer, and a lot of sodium and potassium cause matrix interference [5]. To reduce the interference, the separation technique is necessary.

The techniques of separation and enrichment of trace metal ions in salt and food, such as solvent extraction [6, 7], cloud point extraction [8], coprecipitation [9, 10], and solid phase extraction [11] have been reported. The solid phase extraction (SPE) is applied to enrichment and separation for metal ions, owing to its simple and high preconcentration factor. The copolymer materials with various structures are used in SPE of metal ions owing to their good adsorption properties [12, 13]. For purpose of quantitative adsorption of analytes on sorbents, the metal ions were changed to metal
chelates by utilizing an appropriate chelating agent [14, 15]. However, these sorbents were short of selectivity of Al$^{3+}$, which leads to unable simultaneous enrichment and determination of Al$^{3+}$, Cu$^{2+}$, Cd$^{2+}$ and Pb$^{2+}$ by using ICP-OES.

In this work, a new sorbent of acrylamide-maleic anhydride copolymer was synthesized. The adsorption conditions of Al$^{3+}$, Cu$^{2+}$, Cd$^{2+}$ and Pb$^{2+}$ on the PAMMA were investigated by using SPE technique. The PAMMA could be used several times without its efficiency being affected. The proposed method was used to the enrichment and simultaneous monitoring of Al$^{3+}$, Cu$^{2+}$, Cd$^{2+}$ and Pb$^{2+}$ by ICP-OES in table salt with satisfactory results.

2. Experimental

2.1. Apparatus

An ICP-OES instrument (Optima 2100 DV, USA) was used for metal ions determinations. The axial view mode and the recommended wavelengths were used. The solutions were stirred by magnetic stirrer. The pH of the solutions was measured using a pH meter (Shanghai Lei Ci, China).

2.2. Synthesis of PAMMA sorbent

First, 2.0 g of maleic anhydride, 6.0 g of acrylamide, and 1.2 g of NaOH were dissolved in 40 mL of double-distilled water. Then, 0.2 g of N,N-methylene bisacrylamide cross-linker and 25 mg ammonium persulfate (free-radical initiator) were added under continual stirring. The solution was degassed for 30 min under a nitrogen atmosphere. The reaction vial was sealed and the mixture was put in water bath at 60 °C for 6 h; polymerisation was then completed within 40 min by raising the temperature to 70 °C. The polymerisate was washed three times with double-distilled water and then dried at 90 °C for 24 h. The blocks of polymer were ground and passed through 60 to 100 mesh aperture sieve.

2.3. Procedure

100 mL of sample containing metal ions was placed in 200 mL beaker, and 1 ml of NaAc-HAc solution (pH=5.0) was added, followed by 0.1 g of PAMMA sorbent. The mixture was stirred at 100 rpm for 30 min, and then centrifuged. The sorbent was desorbed with 5.0 mL of 0.3 mol L$^{-1}$ HNO$_3$ for 5 min. The final concentrations of metal ions in desorption solutions were determined with ICP-OES.

3. Results and Discussion

3.1. The effect of pH

Aliquot of 100 mL of the solution including 2.0 μg L$^{-1}$ of Al$^{3+}$, Cu$^{2+}$, Cd$^{2+}$ and Pb$^{2+}$ was tested by using 0.1 g of sorbent under different pH conditions. The sorbent was eluted by 5.0 mL of 0.3 mol L$^{-1}$ HNO$_3$ with agitation for 5 min and then the metal ions were determined and the recoveries were calculated. The recoveries of metal ions increased with increasing pH. Below pH 3.0, the recoveries of metal ions were low due to the protonation of the amino group, but the recoveries increased rapidly above pH 3.0 and were near their maximum values at above pH 4.5. The pH of 5.0 was used for further research.

3.2. The effect of contact time

The different contact times were studied at 100 rpm for their respective recoveries of metal ions. The metal ion recoveries were greater than 92% even if the adsorption process was performed for 30 min. Therefore, a contact time of 30 min was optimum adsorption equilibrium time.

3.3. The effect of elution condition

The elution of the analyte from the sorbent containing metal ions was tested by using 5.0 mL of different concentrations of HCl or HNO$_3$ as eluent. It was found that metal ions could be quantitatively
desorbed with 5.0 mL of 0.3 mol L\(^{-1}\) HNO\(_3\) solution. When HNO\(_3\) was used as a desorption solution, the quantitative recoveries (> 92%) can be obtained. The time for desorption of Al\(^{3+}\), Cu\(^{2+}\), Cd\(^{2+}\) and Pb\(^{2+}\) was changed from 1 to 10 min, the results indicated that target ions could be quantitatively eluted at 5 min. Therefore, 5.0 mL of 0.3 mol L\(^{-1}\) HNO\(_3\) solution was used as the eluent and an elution time of 5 minutes was selected for subsequent experiments.

3.4. Calibration curve, detection limit, and precision
Under optimal experimental conditions, standard mixture solutions (0.6 μg L\(^{-1}\) - 300.0 μg L\(^{-1}\)) were concentrated and measured simultaneously according to the procedure. The limits of detection were 0.31, 0.26, 0.43, and 0.12 μg L\(^{-1}\), and the RSD (n=6) was 1.5%, 3.7%, 3.0%, and 2.6% for Al\(^{3+}\), Cu\(^{2+}\), Cd\(^{2+}\) and Pb\(^{2+}\), respectively. This method showed low limit of detection and high reproducibility.

3.5. Analysis of sample
This method was used for the detecting of Al\(^{3+}\), Cu\(^{2+}\), Cd\(^{2+}\) and Pb\(^{2+}\) in table salts by ICP-OES. The results were summarized in Table 1. The recoveries of analytes were between 95.0 and 103%.

4. Conclusions
In the presented work, a sensitive and selective method was proposed for simultaneous determining of Al\(^{3+}\), Cu\(^{2+}\), Cd\(^{2+}\) and Pb\(^{2+}\) by ICP-OES in salt based on acrylamide-maleic anhydride copolymer as a solid phase extractant. This method could be used to quantitative preconcentration of the analytes from saline solution. The synthesis of PAMMA is relatively simple and no pollution. The results showed that this method was simple, sensitive and reliable.

| Salt               | Ion  | Concentration (μg g\(^{-1}\)) | Recovery (%) |
|--------------------|------|------------------------------|--------------|
|                    |      | Added | Found        |              |
| Refined salt       | Al\(^{3+}\) | 0     | 0.219 ± 0.01\(^a\) | 98.5         |
|                    |      | 0.2   | 0.416 ± 0.009 |              |
|                    | Cu\(^{2+}\) | 0     | 0.191 ± 0.003 | 98.0         |
|                    |      | 0.2   | 0.387 ± 0.007 |              |
|                    | Cd\(^{2+}\) | 0.05  | 0.095 ± 0.008 | 98.0         |
|                    |      | 0     | 0.0890 ± 0.02 |              |
|                    | Pb\(^{2+}\) | 0.1   | 0.185 ± 0.01  | 96.0         |
| crushing baysalt   | Al\(^{3+}\) | 0     | 0.0940 ± 0.005 | 95.0         |
|                    |      | 0.1   | 0.189 ± 0.002 |              |
|                    | Cu\(^{2+}\) | 0     | 0.259 ± 0.05  | 96.7         |
|                    |      | 0.3   | 0.549 ± 0.02  |              |
|                    | Cd\(^{2+}\) | 0     | 0.238 ± 0.03  | 101          |
|                    |      | 0.3   | 0.542 ± 0.01  |              |
|                    | Pb\(^{2+}\) | 0.5   | 0.374 ± 0.09  | 103          |
| solar salt         | Al\(^{3+}\) | 0     | 0.173 ± 0.05  | 98.0         |
|                    |      | 0.2   | 0.369 ± 0.02  |              |
|                    | Cu\(^{2+}\) | 0     | 0.867 ± 0.03  | 98.7         |
|                    |      | 1     | 1.854 ± 0.01  |              |
|                    | Cd\(^{2+}\) | 0     | 0.0790 ± 0.005 | 103          |
|                    |      | 0.1   | 0.182 ± 0.003 |              |
|                    | Pb\(^{2+}\) | 0.3   | 0.268 ± 0.02  | 99.3         |

\(^a\) Mean± standard deviation.
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References
[1] P. N. Nomngongo, J. C. Ngila, T. A. M. Msagati, B. Moodley, Preconcentration of trace multi-elements in water samples using Dowex 50W-x8 and Chelex-100 resins prior to their determination using inductively coupled plasma atomic emission spectrometry (ICP-OES), Phys. Chem. Earth. 66 (2013) 83-88.
[2] F. L. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: A review, J. Environ. Manage. 92 (2011) 407-418.
[3] S. Tontrong, S. Khonyoung, J. Jakmunee, Flow injection spectrophotometry using natural reagent from Morinda citrifolia root for determination of aluminium in tea, Food Chem. 132 (2012) 624–629.
[4] R. Verma, B. D. Gupta, Detection of heavy metal ions in contaminated water by surface a) plasmon resonance based optical fibre sensor using conducting polymer and chitosan, Food Chem. 166 (2015) 568-575.
[5] M. Hoenig, H. Dočekalová, H. Baetena, Study of matrix interferences in trace element a) analysis of environmental samples by inductively coupled plasma atomic emission spectrometry with ultrasonic nebulization, J. Anal. At. Spectrom. 13 (1998) 195-199.
[6] F. A. C. Amorim, S. L. C. Ferreira, Determination of cadmium and lead in table salt by sequential multi-element flame atomic absorption spectrometry, Talanta 65 (2005) 960-964.
[7] H. Sereshi, S. Bakhtiari, V. Khojeh, Simultaneous determination of aluminium, copper, iron and zinc in Oscillatoria, Juncus littoralis tissues and wetland water samples by ultrasound-assisted emulsification-microextraction combined with ICP-OES, Anal. Methods 3 (2011) 2936-2942.
[8] A. B. Tabrizi, Cloud point extraction and spectrofluorimetric determination of aluminium and zinc in foodstuffs and water samples, Food Chem. 100 (2007) 1698-1703.
[9] S. Kagaya, T. Mizuno, K. Tohda, Inductively coupled plasma atomic emission spectrometric determination of 27 trace elements in table salts after coprecipitation with indium phosphate, Talanta 79 (2009) 512-516.
[10] D. S. K. Peker, O. Turgoglu, M. Soylak, Dysprosium(III) hydroxide coprecipitation system for the separation and preconcentration of heavy metal contents of table salts, J. Hazard. Mater. 143 (2007) 555-560.
[11] V. Camel, Solid phase extraction of trace elements, Spectrochim. Acta. B. 58 (2003) 1177-1233.
[12] M. Soylak, I. Murat, Determination of copper, cobalt, lead, and iron in table salt by FAAS after separation using violuric acid and multiwalled carbon nanotubes, Food Anal. Method 5 (2012) 1003-1009.
[13] G. R. Kiani, H. Sheikholes, N. Arsalani, Heavy metal ion removal from aqueous solutions by functionalized polyacrylonitrile, Desalination 269 (2011) 266-270.
[14] M. Ceglowski, G. Schroeder, Removal of heavy metal ions with the use of chelating polymersobtained by grafting pyridine–pyrazole ligands onto polymethylhydrosiloxane, Chem. Eng. J. 259 (2015) 885-893.
[15] M. H. Karbasi, B. Jahanparast, M. Shamsipur, J. Hassan, Simultaneous trace multielement determination by ICP-OES after solid phase extraction with modified octadecyl silica gel, J. Hazard. Mater. 170 (2009) 151-155.