Preconcentration Of Heavy Metal Cations On The Polymeric Sorbent Prior To Their Determination By Atomic Absorption Spectrophotometery

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ABSTRACT

An efficient polymeric sorbent (poly(ethylenglycoldimethacrylate-co-methacrylic acid) (EGDMA-co-MAA)) was prepared, conditioned and used in adsorption of cations as oxinate complexes. The extent linear dynamic ranges and lower limits of detection are the advantages of the proposed methods. The relative standard deviations (RSD%) obtained are less than 8% for all cations. Interferences studies were also carried out using different matrices and found that most of them have no evil effect on the recovery of the analytes. Finally this method was applied to determine heavy metals content of different samples at µg/L level. After optimizing parameters affecting adsorption of target analytes such as sample size, pH, kind of buffer, elution solvent, etc column technique was used to preconcentraton of those compounds followed by their determination using flame atomic absorption spectrophotometry.
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INTRODUCTION

Metals are unique among pollutants that cause adverse health in that they occur naturally and, in many instances, are ubiquitous in the environment.

Regardless of how metals are used in consumer products or industrial processes, some level of human exposure is, in most instances, inevitable. Furthermore, many are biologically essential but become toxic with increasing dosage. The problem for the

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toxicologist, therefore, is to be able to recognize the adverse effects. Metals are an important emerging class of human carcinogens. At least five transition metals or metalloids, in one form or another, are accepted as human carcinogens by the international agency for research on cancer. Several more metals and/or their compounds are suspected to have carcinogenic potential in humans[1-3]. Considering that the list of definitive human carcinogens is rather small[4], it is clear that metals, as a class, make up a substantial portion of the compounds known to have human carcinogenic potential. Many metals are also very potent carcinogens in laboratory animals[5,6]. There is several exposure situations associated with metal carcinogenesis in humans[7–10]. Most of these involve occupation in metal refining, smelting, or other metal processing. Iatrogenic metal carcinogenesis can occur, and certain archaic[11] and contemporary[4] medical metals preparations are probably human carcinogens. Exposures that occur during chemical production using metals, such as for certain chromium pigments, have been associated with human cancer[5]. Individuals involved in certain mining processes and in iron and steel founding may be at greater risk for metal-induced carcinogenesis, although exposures to nonmetallic agents likely are important in such cases[4]. Metallic fumes generated during welding are probably carcinogenic to humans[5]. Many other occupational activities or metals could be found in the future to pose similar risks. There are also some cases in which environmental exposures to metals have been linked to human cancer, but these are limited[4, 6].

Atomic absorption spectrometer (AAS) is generally main instrument of analytical chemistry laboratories for the determination of traces heavy metal ions, due to its relatively low cost. However the main two problems for the determination of heavy metal ions by AAS are low levels of metal ions and interferic influences of main components of samples. In order to solve these problems, the separation/preconcentration procedures including solid phase extraction[12-18], membrane filtration[19], electroanalytical techniques[20,21], solvent extraction[22] and ion-exchange[23] are a necessity. The usages of synthetic adsorption polymers on the solid phase extraction

of traces heavy metal ions are also very popular[24, 25-31]. In general, metal chelates in the aqueous solutions were adsorbed on the polymer and then desorbed with a suitable eluent solution.

In previous works [32-35], we used natural by-products such as rice and wheat brans in removal or preconcentration of heavy metals from aqueous media. Some advantages such as low expensive and no need to recovery after use, are the main advantages of these sorbents. But they have low capacity towards cations. Additionally different mechanisms such as ion exchange, complex formation, etc. play simultaneously roles in the adsorption of cations. In this study poly (EGDMA-co-MAA) copolymer was synthesized and used in preconcentration of cations prior to their determination by flame atomic absorption spectrophotometer. High affinity of polymer towards cations (as oxinate complexes) leads to preconcentration factor 100 is achievable which allows determination of studied cations at μg/L level is feasible.

EXPERIMENTAL

Chemicals and solutions

Chemicals for the polymer synthesis were azo-N,N -bisisobutyronitrile (AIBN) (Janssen), methacrylic acid (MAA), ethyleneglycol dimethacrylate (EGDMA), methanol and chloroform (all from E. Merck). Other compounds such as HNO_3, HCl, H_2SO_4, $NaCl$, $Cr(NO_3)_3 \cdot 9H_2O$, $Cd(NO_3)_3 \cdot 4H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Pb(NO_3)_2$, $Ni(NO_3)_2 \cdot 6H_2O$, metallic copper, NaOH ,etc were pro-analysis grade and purchased from E.Merck company (Darmstadt, Germany).

Individual standard solution of cations (1000 mg/L) was prepared by dissolving nitrate of cations in distilled water in which a few drops of concentrated nitric acid was added or dissolving pure metals in concentrated nitric acid and dilution to 100 mL with distilled water. Ammonium acetate buffer (C = 1 M, pH = 7.0) and 0.1 M oxine in methanol were used.

Apparatus

An LKB Uv-Vis spectrophotometer (model

4045) and a Shimadzu atomic absorption/emission spectrophotometer (model AA-670G) were used in absorbances measurement of oxine and cations, respectively. pH measurements were carried out using a WTW pH-meter (Multilab 504, Germany).

Polymer synthesis

For the preparation of the sorbent polymer, the functional monomer (MAA, 4.0 mmol, 0.34 mL), the cross-linking monomer (EGDMA, 20.0 mmol, 3.8 mL) and the initiator (AIBN, 0.24 mmol, 40.0 mg) were dissolved in 5.6 mL of chloroform. The polymerization mixture was degassed with nitrogen for 5 min and placed at 50°C in thermostated water bath. The reaction was allowed to proceed for 24 h. Finally, the tube was crushed, the polymer was ground and sieved, and the particle size fraction of ≤150 μm (100 mg) was placed into a small glass column (5 cm × 0.4 cm i.d.). Two filter disks were placed on the bottom and up of the polymer beads. In order to extract the unreacted monomers, this fraction was washed with 10 mL methanol. The polymer was used without drying to adsorb the studied cations as oxinate complexes.

Adsorption capacity of polymer

In order to determine the adsorptive capacity of polymer 3 mL fractions of 10^{-3} M oxine solution in distilled water were passed through the column filled with 100 mg of polymer (particle size <150 μm). Absorbance of these solutions were recorded at wavelength 390 nm after passing through the column and compared to that of 10^{-3} M oxine solution.

Procedure

To 100 mL solution of cations (Cu^{2+} 1, Fe^{3+} 0.5, Ni^{2+} 1, Co^{2+} 0.5, Mn^{2+} 0.3, Cr^{3+} 1, Zn^{2+} 0.05, Cd^{2+} 0.05 and Pb^{2+} 1 mg/L), 5 mL ammonium acetate buffer (C = 1 M, pH = 7.0) and 5 mL 0.1 M oxine in methanol were added and stirred by magnetic stirrer. The obtained solution was passed through a small glass column (10 cm × 0.4 cm i.d.) filled with 100 mg polymer beads (<150 μm) fitted by two filter disks. Flow rate was adjusted at about 5 mL/min by suction system .The adsorbed analytes on the sorbent beads were washed with 3 mL 1 M HNO_3 and its absorbance was read at different wavelengths us-

ing suitable hollow cathode lamps.

RESULTS AND DISCUSSION

Optimization of experimental conditions

Different parameters such as pH, buffer type, particle size and weight, sample size, kind and volume of elution solvent, salting out effect, flow rate of sample, etc play important roles and optimized before using sorbent for preconcentration of the studied cations. pH is mainly effective on the reaction between oxine and cations to produce neutral and bulk oxinate complexes of cations which are adsorbed by the polymeric sorbent. Different pH over the range 1-9 were tested and found that pH = 7 can be selected as optimum pH (Figure 1). At lower pH oxine protonated by H^+ ions and the oxinate complexes were not quantitatively formed. It is evident that the relatively stable complexes such as Fe^{3+} and Cu^{2+} complexes can be produced even at pH = 3. At higher than pH = 8 hydroxide ions interference is to be serious and formation and adsorption of cations onto the sorbent is decreased. Other parameters, which have important roles in this study, are volume and kind of elution solvent. Methanol and 1 M HNO_3 were used for this purpose. Both of them were good elution systems with a little preference of HNO_3 over the methanol. To select the optimum volume of solvent after adsorption of analyst on the polymer, it was washed with 1M HNO_3 in 0.5 mL fractions and
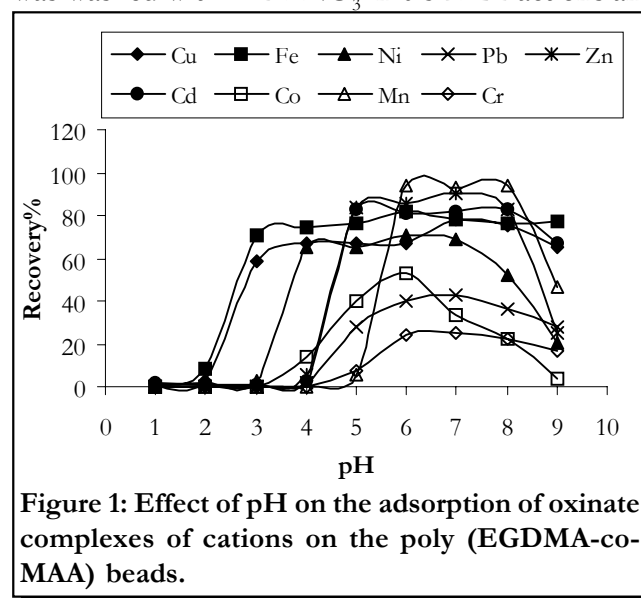

Figure 1: Effect of pH on the adsorption of oxinate complexes of cations on the poly (EGDMA-co-MAA) beads.
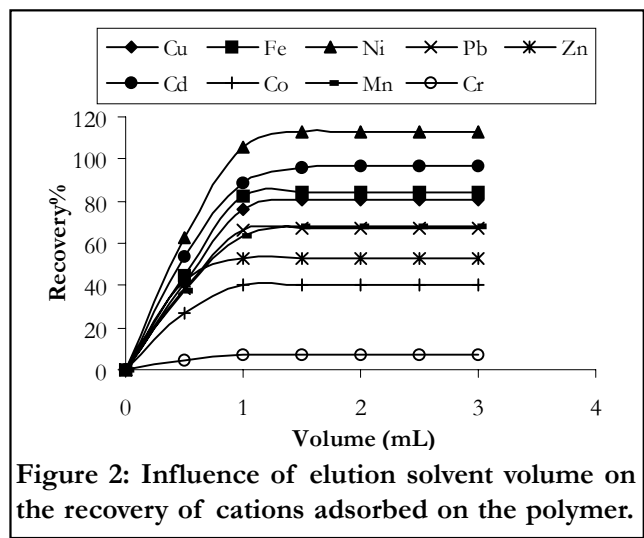
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Figure 2: Influence of elution solvent volume on the recovery of cations adsorbed on the polymer.

Figure 3: Capacity of polymeric sorbent toward oxine.

TABLE 1: The selected experimental conditions

Parameter	Amount or kind	Parameter	Amount or kind
Sample size	100 mL	pH	7.0
Amount of sorbent	100 mg	Buffer	Ammonium acetate (1 M)
Elution solvent	1 M HNO₃	Salting out agent	NaCl in 1 M concentration
Volume of elution solvent	3 mL	Flow rate of sample	5 mL/min
Particle size	<150 μm	-	-

the recovered cations in percent were plotted vs. volume of solvent in figure 2. These results show that all profiles reached to plateau at 1 mL and remained constant. This is important due to access high preconcentration factor. By using 100 mL solution preconcentration factor of 100 is achievable. However due to using flame atomic absorption spectrophotometer as detection system we need at least 3 mL solution. For this reason 3 mL was selected as volume of elution solvent. In order to summarize, other experimental conditions are included in TABLE 1.

Evaluation of sorbent capacity

Capacity of sorbent was evaluated by passing oxine through the column filled with 100 mg polymer. Adsorbed percent of oxine on the polymer as a function of volume of oxine solution is plotted in figure 3. Oxine in the first 54 mL solution was completely adsorbed by the polymer, which shows that capacity of polymer towards oxine is high. After saturation of polymer by oxine, it was washed with
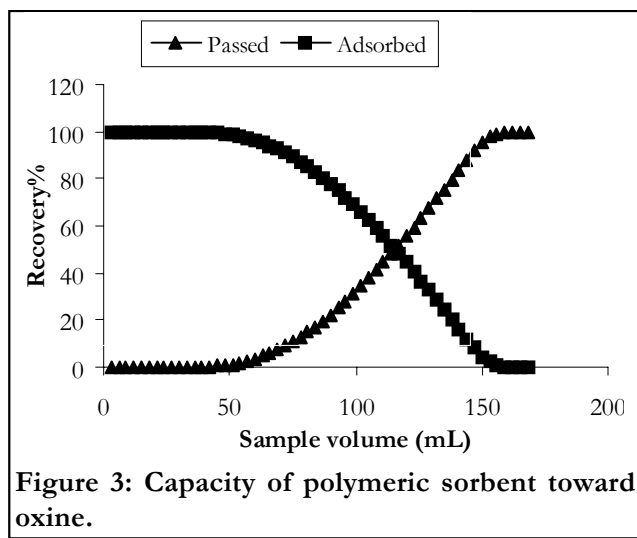
methanol and its absorbance was recorded against pure methanol as a blank solution. By comparing absorbance of this solution with those of standard solutions of oxine in methanol, capacity of polymer in adsorption of oxine were obtained 1.17 mmol/g or 170 mg/g.

Analytical characteristics of the proposed method

Different features of the analytical method (determination of heavy metal cations after preconcentration on the polymeric sorbent) such as calibration curves equations, linear dynamic ranges, correlation coefficients and the limits of detection (LOD) were evaluated and summarized in TABLE 2. Extant linear dynamic ranges with low limits of detection (0.7 - 20 μg/L) as well as correlation coefficients higher than 0.990 indicated that the proposed method have most of criteria required for a sensitive analytical technique. The repeatability of the method was also assessed by experiments performed on the similar solutions. Data in TABLE 3 show that all cations (expect Cr^{3+}) are recovered more than 60% by the studied method. Some cations such as Fe^{3+}, Mn^{2+}, Pb^{2+} and Cd^{2+} have recoveries nearly 100%. The repeatability of the method is good and relative standard deviation (RSD%) for five repeated experiments is less than 8% for all cations.

Application of the method to real sample

In order to illustrate efficiency of the method, heavy metal content of different samples were determined by this method. Clear samples such as tap water to dirty samples such as municipality waste-

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TABLE 2: Analytical features of the proposed method

Cation	Calibration curve equation	Linear dynamic range (μg/L)	Correlation coefficient ®	Limit of detection (μg/L)
Cu^{2+}	A = 0.0007C + 0.0592	10 - 2500	0.994	3
Cr^{3+}	A = 0.00005C - 0.0065	50 - 5000	0.994	20
Fe^{3+}	A = 0.0004C + 0.0087	25 - 2000	0.995	8
Mn^{2+}	A = 0.0002C + 0.0062	15 - 1200	0.994	5
Pb^{2+}	A = 0.0001C + 0.0069	50 - 4000	0.999	20
Cd^{2+}	A = 0.0039C + 0.0093	2 - 250	0.997	0.7
Co^{2+}	A = 0.0004C - 0.0012	25 - 2000	0.995	8
Ni^{2+}	A = 0.0006C + 0.0739	50 - 1500	0.990	20
Zn^{2+}	A = 0.0033C + 0.0214	2.5 - 250	0.995	0.8

TABLE 3: Recovery and repeatability study

Cation	Recovery					Mean recovery ± standard deviation	Relative standard deviation (RSD%)
	1	2	3	4	5		
Cu^{2+}	83.6	73.4	74.6	73.2	71.3	75.2 ± 4.83	6.42
Cr^{3+}	14.5	15.0	14.5	15.0	15.0	14.8 ± 0.27	1.82
Fe^{3+}	99.3	106.0	102.7	102.7	99.3	102.0 ± 2.81	2.75
Mn^{2+}	102.0	112.0	102.0	109.0	112.0	107.4 ± 5.08	4.73
Pb^{2+}	104.0	104.0	96.6	96.6	93.7	99.0 ± 4.73	4.78
Cd^{2+}	105.4	100.0	97.3	100.0	97.3	100.9 ± 3.69	3.66
Co^{2+}	67.5	61.9	59.4	56.1	59.2	60.8 ± 4.26	7.01
Ni^{2+}	88.8	89.1	89.6	89.5	89.8	89.4 ± 0.40	0.45
Zn^{2+}	80.5	92.5	91.1	80.1	79.4	84.7 ± 6.49	7.66

TABLE 4: Concentration of cations (μg/L) in different samples obtained by the proposed method. Data are mean of three repeated experiments.

Cation	Sample				
	Tap water	Well water	River water	Urmia lake water	Municipality wastewater
Cu^{2+}	27.6	34.9	37.0	17.5	60.8
Cr^{3+}	ND^a	ND	ND	ND	ND
Mn^{2+}	323	561	819	221	604
Cd^{2+}	1.05	1.96	2.32	2.66	1.59
Ni^{2+}	115	178	114	57.4	140
Pb^{2+}	ND	ND	ND	ND	ND
Zn^{2+}	108	41.1	38.2	22.7	103
Fe^{3+}	115	170	95.9	61.2	90.4
Co^{2+}	12.2	ND	17.8	26.0	80.8

[a] Not detected

(TABLE 4). To evaluate precision of the method the added–found method was used. The above–mentioned samples were selected and the studied cations were added to them at three concentrations. The recoveries were calculated and compared to those obtained from samples prepared in distilled water. The results in TABLE 5 show that in most samples, excluding Urmia lake water, the deviation from ideal value (100%) is negligible. However this method can be useful for determination of heavy metals in most matrices at μg/L by using flame atomizer system.

water as well as high complex matrix sample such as Urmia lake water (brine water having more than 25% salt) were selected for this purpose. Most of cations were found in these samples on the range of μg/L

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TABLE 5: Comparative studies of obtained recoveries for cations in different samples in comparison with those obtained from distilled water.

Cation	Conc. mg L^{-1}	Sample				
		Tap water	Well water	River water	Urmia lake water	Municipality Wastewater
Cu^{2+}	2.5	86.7	84.3	93.2	87.7	91.5
	5.0	108	93.5	109	43.2	110
	7.5	96.2	102	96.7	26.2	107
		97.0 ± 10.67[a]	93.3 ± 8.85	99.6 ± 8.30	52.4 ±31.8	103 ± 9.93
Cr^{3+}	5	87.1	85.1	120	187	60.3
	10	89.0	97.0	133	197	86.0
	15	70.6	75.7	105	82.1	80.7
		82.2 ± 10.12	85.9 ± 10.67	119 ± 14.01	155 ± 63.6	75.7 ± 13.6
Cd^{2+}	0.25	104	114	112	56.6	96.2
	0.50	99.3	99.3	101	30.8	90.4
	0.75	98.1	105	97.1	25.3	92.8
		100 ± 3.12	103 ± 7.41	103 ± 7.73	37.6 ±16.7	93.1 ± 2.91
Ni^{2+}	5	92.3	90.5	91.8	86.7	83.5
	10	103	101	103	42.0	99.8
	15	100	99.4	101	29.2	94.7
		98.4 ± 5.52	97.0 ± 5.66	98.6 ± 5.97	52.6 ± 30.2	92.7 ± 8.34
Pb^{2+}	5	105	113	116	24.0	101
	10	106	94.6	110	17.2	102
	15	9309	106	98.2	14.3	97.8
		102 ± 6.72	104 ± 9.29	108 ± 9.06	18.5 ± 4.98	100 ± 2.19
Zn^{2+}	0.25	220	117	63.2	71.9	95.4
	0.50	142	92.3	70.6	29.4	93.6
	0.75	121	99.1	78.1	21.2	99.6
		161 ± 52.2	103 ± 12.8	70.6 ± 7.45	40.8 ± 27.2	96.2 ± 3.08
Fe^{3+}	2.5	111	78.8	83.0	70.5	85.8
	5.0	101	85.9	94.8	25.7	94.8
	7.5	94.8	80.6	102	20.5	94.8
		102 ± 8.17	81.8 ± 3.69	93.3 ± 9.59	38.9 ± 27.5	91.8 ± 5.20
Co^{2+}	2.5	113	105	100	71.1	80.8
	5.0	99.2	94.1	83.5	32.9	66.7
	7.5	103	105	87.7	21.9	73.9
		105 ± 7.13	101 ± 6.29	90.4 ± 8.57	42.0 ± 25.8	73.8 ± 7.05
Mn^{2+}	1.5	111	108	61.7	125	105
	3.0	103	88.9	73.3	37.8	93.2
	4.5	98.3	103	68.3	38.1	110
		104 ± 6.42	100 ± 9.90	67.8 ± 5.82	67.0 ± 50.3	103 ± 8.63

[a] Mean recovery ± standard deviation

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CONCLUSIONS

In this study, poly (ethyleneglycoldimethacrylate-co-methacrylic acid) was synthesized and used as sorbent for heavy metals. Precomplexation of cations was carried out prior to contact with polymer beads in column experiments. Four cations (Fe^{3+}, Mn^{2+}, Pb^{2+} and Cd^{2+}) were recovered nearly 100%. In adsorption and desorption of cations from the polymer preconcentration factor of 100 is achievable and caused that the sensitivity of method using flame atomic spectrophotometer as detection system is to be comparable with that of electrothermal atomic absorption technique.

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