

Synthesis of A Novel Chelating Resin Functionalized with β -Dicarbonyl Units From A New Monomer and Its Use for Selective Separation and Preconcentration of Some Trace Metals In Water Samples

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ABSTRACT: A new chelating resin, poly(4-ethoxy-2,4-dioxobutyl 2-methylacrylate), functionalized with β -dicarbonyl units derived from a newly synthesized monomer was prepared and characterized with molecular spectroscopic methods. The synthesized polymer was used for the separation and preconcentration of Mn(II), Co(II), Ni(II), Zn(II), and Pb(II) ions before their determination by flame atomic absorption spectrometry. The effects of different parameters, such as pH of sample solution, sample and eluent flow rates, volumes of sample and eluent, concentration and type of eluent, and matrix ions on quantitative recovery of the analytes were evaluated for optimal experimental conditions. The adsorption capacities of the chelating resin for cobalt(II) and nickel(II) were found to be 24.2 and 19.8 mg g⁻¹, respectively. Validation studies for the proposed method were performed using three certified reference materials, and the results obtained were agreed with those of the certified values. The proposed method was successfully applied to the analysis of water samples. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: β -dicarbonyl compounds; chelating polymer; preconcentration; trace metal; solid phase extraction

Received 15 July 2011; accepted 19 April 2012; published online

DOI: 10.1002/app.37938

INTRODUCTION

As the number of ecological and health problems associated with environmental contamination continues to rise, the determination of trace amounts of heavy metal ions in environmental samples is gaining importance.¹ Despite the selectivity and sensitivity of conventional analytical techniques such as atomic absorption spectrometry, there is a crucial need for the separation and preconcentration of trace elements before their analyses due to low concentrations and matrix effects in numerous samples.

In solid phase extraction (SPE), polymers that have a chemical affinity with metal ions are important as collectors and suitable for metal ion enrichment before their determination by AAS. For the selectivity and sensitivity of SPE, many types of polymeric metal ion collectors functionalized with various chelating structures have been developed. Generally, these polymers have amino,^{2,3} azo,^{2,4,5} hydroxyl,^{5–7} or carboxylic acid^{8,9} groups at suitable positions.

There are two methods for the preparation of chelating polymers as solid phase extractors. First, chelating units are immo-

bilized on corresponding support materials, such as Amberlite resins. Immobilization methods, however, possess an important disadvantage due to the insolubility of the crude resin. Therefore, the process of purification and standardization of immobilized resins is restricted. Although synthesis of chelating monomers and polymerization is straightforward, many chelating groups of monomers, such as phenolic-OH or $-\text{N}=\text{N}-$, might prevent the radical polymerization of the monomers.¹⁰ It seems, however, that this method is more convenient than the immobilization method to prepare chelating polymers with respect to standard physical and chemical properties.

Among the chelating molecules, compounds functionalized with a β -dicarbonyl group are well-known as universal chelating agents in chemistry. The capability of the β -dicarbonyl containing polymers to undergo chelation with metal ions, however, has yet to be considered for SPE as an adsorbent. According to published reports, some metal complexes of polymer functionalized with β -dicarbonyl units have been suggested as heterogeneous catalysts in olefin oxidation.^{11–13} In addition, some coating metallic substrates with polymers, including β -dicarbonyl moiety, have demonstrated improved corrosion resistance.¹⁴

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The aim of this article was to synthesize a new chelating resin based on poly(4-ethoxy-2,4-dioxobutyl-2-methylacrylate), [poly(EDM)], functionalized with β -dicarbonyl units and characterized by molecular spectroscopic methods. The applicability of the obtained ion exchanger for separation and preconcentration of Mn(II), Co(II), Ni(II), Zn(II) and Pb(II) ions from waters before their determination was studied using the flame atomic absorption spectrometry (FAAS). It was also studied the effect of such parameters as pH of sample solution, sample and eluent flow rates, volumes of sample and eluent, concentration and type of eluent, as well as kind of matrix on removal of Pb(II), Co(II), Ni(II), Zn(II), and Pb(II) ions. Optimal conditions of quantitative recovery of the above mentioned heavy metal ions were determined. The validation studies for the proposed method were performed using certified reference materials and the obtained results were agreed with those of certified values.

EXPERIMENTAL

Instrumentation

A PerkinElmer model AAnalyst 800 flame atomic absorption spectrometer (Waltham, MA, USA) was used for the determination of the metals. The operating parameters for the spectrometer were set as recommended by the manufacturer. All of the absorbance measurements were carried out in air and acetylene flow rates of 283 and 33 cm³ s⁻¹, respectively. A Consort C533 model digital pH meter (Belgium) was used for all the pH measurements. ¹H (300.13 MHz) and ¹³C (75.47 MHz) NMR spectra were obtained on Bruker Avance III 400 Ultrashield NMR spectrometer (Bruker GmbH, Rheinstetten, Germany). Infrared spectra of the synthesized materials were measured on a Jasco 460 Plus FT-IR spectrometer (Jasco Co., Tokyo, Japan). Elemental analyses were carried out by a Leco CHNSO-932 automatic analyser (USA). Thermal data were obtained by using a Setaram Labsys TG-DSC/DTA thermobalance in N₂ atmosphere.

Reagents and Solutions

All chemicals were of analytical reagent grade. Distilled-deionized water was used in all experiments. Stock solutions (1000 mg dm⁻³) of the elements were prepared by dissolving appropriate amounts of their nitrate salts in 0.15 mol dm⁻³ HNO₃ and further diluted daily before use. Ethyl 4-chloroacetoacetate was used as purchased. The following buffer solutions were used for the SPE procedures: CH₃COOH/CH₃COONa buffer for pH 4–6; Na₂HPO₄/NaH₂PO₄ buffer for pH 7–8; and NH₃/NH₄Cl buffer for pH 8–10. Poly(EDM) was prepared at 200–300 mesh particle size as broken pieces. Before use, it was washed with hydrochloric acid, ethanol, and acetone; then it was rinsed with water until a neutral solution was obtained, and then it was dried at room temperature. Synthetic sea water (SSW) was prepared from 23.479 g NaCl, 4.981 g MgCl₂, 3.917 g Na₂SO₄, 1.102 g CaCl₂, 0.664 g KCl, 0.192 g NaHCO₃, 0.096 g KBr, 0.026 g H₃BO₃, 0.024 g SrCl₂, 0.030 g NaF in a 1000 cm⁻³ volumetric flask.¹⁵ Certified reference materials (water) were purchased from the Canada National Water Research Institute.

Synthesis of 4-ethoxy-2,4-dioxobutyl 2-methylacrylate as Monomer

A mixture of ethyl 4-chloroacetoacetate (0.02 mol, 3.30 g), sodium methacrylate (0.20 mol, 2.20 g), of triethylbenzylammo-

niumchloride (TEBAC) (0.20 g) and NaI (0.01 g) in 50 cm³ of acetonitrile was placed in a two-neck round bottom flask equipped with a magnetic stirrer and a thermometer. The mixture was stirred at 60°C for 5 h. The reaction mixture was transferred to a separating funnel and extracted with 30 cm³ of diethyl ether/distilled water mixture (1 : 1). The organic extract was dried (MgSO₄). The solvent was filtered. The filtrate was removed on a rotary evaporator. The monomer was obtained as brown oil. C₁₀H₁₄O₅, yield: 3.56 g (77%). ¹³C NMR (CDCl₃): δ = 196.9, 166.4, 166.2 C=O, 135.2 CH₂=C, 126.9 CH₂=C, 67.9, 61.5 OCH₂, 46.0 COCH₂CO, 18.0, 13.9 ppm CH₃. IR (KBr): 1752, 1727 (esters and ketone's C=O), 1637 cm⁻¹ (C=C).

High purification of 4-ethoxy-2,4-dioxobutyl 2-methylacrylate (EDM) for spectroscopic analysis: A solution of EDM 2.140 g (0.010 mol) in methanol (30 cm³) and Cu(OAc)₂ (0.090 g, 0.005 mol) was stirred for 10 min at room temperature. After solvents were removed by filtration, the products Cu(EDM)₂ were washed with water and acetone. The Cu(EDM)₂ was transferred to a separating funnel and extracted with 100 cm³ of diethyl ether/1 mol dm⁻³ HCl mixture (1 : 1). The organic extract was dried with MgSO₄ and filtered. The filtrate was removed on a rotary evaporator, and pure monomer was obtained as a brown oil.

Synthesis of Poly(EDM) as Sorbent

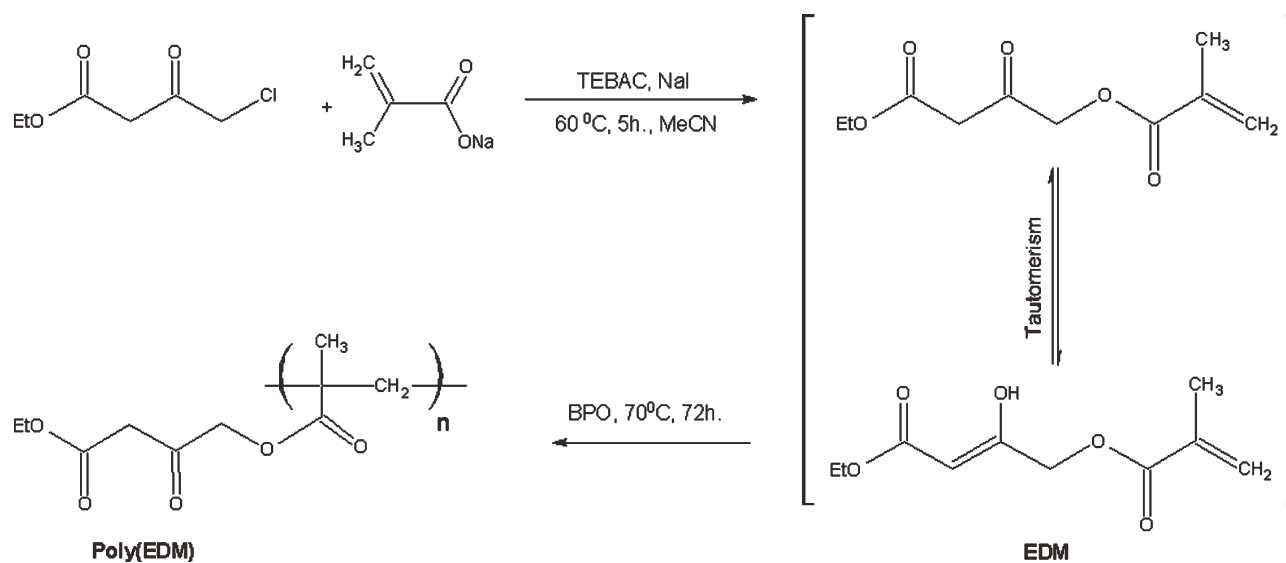
Polymerization reactions of EDM (4.280 g, 0.020 mol) were carried out in 25 cm³ of 1,4-dioxane using benzoyl peroxide (BPO, 0.010 g) as an initiator in a sealed tube. The reaction mixtures were purged for about 5 min before heating, and then the mixture was heated to 70°C for 4 days in an oil bath. The mixtures were cooled to room temperature and slowly poured, with constant stirring, into a large excess of tetrahydrofuran (THF). The viscous polymer was purified by repeated precipitation with the THF and finally dried under vacuum for 3 days. The polymer was obtained as yellow solid. Yield: 3.560 g (83%). IR (KBr): 3500 cm⁻¹ (br., OH, enol), 1735 cm⁻¹ (C=O, esters). Calcd. C, 56.07; H, 6.59; found C, 55.96; H, 6.87. T_g: 49°C.

Preparation of Poly(EDM) Column

About 0.50 g of poly(EDM) was packed in a glass column. The column was treated with buffer solution (100 cm³, pH 10), 3 mol dm⁻³ HCl and HNO₃ (50 cm³) and washed with doubly distilled water until free from acid.

Proposed Preconcentration Procedure

The method was tested with model solutions before the determination of the trace metals in the real samples. The pH of model solutions (50 cm³) containing 10 μ g Ni(II) and Co(II), 2.5 μ g Zn(II), 5 μ g Mn(II), and 20 μ g Pb(II) ions was adjusted to 8.5. The model solution was then passed through the column containing the poly(EDM) chelating resin at a flow rate of 0.025 cm³ s⁻¹. The trace metal ions retained on the column were eluted by using 5 cm³ of 1 mol dm⁻³ HCl solution. The concentration of the metal ions in the eluate was determined by FAAS. A blank solution was run under the same conditions without adding the analytes. The adsorbent was used repeatedly after washing with water and then conditioned with the buffer solution.



Scheme 1. Synthetic route of EDM and poly(EDM).

Sample Pretreatment

The sewage water sample from the campus area of Bozok University, Yozgat, Turkey was immediately filtered through a Millipore cellulose membrane filter (0.45 μm pore size), acidified to pH 2 with HNO_3 and stored in precleaned polyethylene bottles. The proposed procedure was applied to aliquots of 200 cm^3 of the sewage water.

RESULTS AND DISCUSSION

Synthesis of EDM and Poly(EDM)

A nucleophilic substitution reaction of ethyl 4-chloroacetoacetate and sodium methacrylate was carried out with TEBAC as a phase transfer catalysis and NaI as catalyst in CH_3CN . The reaction (at 60 °C) was completed in less than five hours and gave a 77% yield of substitution product, EDM (Scheme 1). Polymerization of EDM was carried out in 1,4-dioxane using BPO as initiator in a sealed tube.

Spectroscopic Characterizations of EDM and Poly(EDM)

In the ^1H NMR spectra of EDM, the characteristic shifts of CH_3 protons at 1.26 (t, $J = 7.3$ Hz) and 1.94 ppm, CH_2 protons of methacrylate section at 6.18 and 5.65 ppm, COCH_2CO protons at 3.49 ppm, OCH_2 protons at 4.81 and 4.17 (q, $J = 7.4$ Hz) were observed. The OH proton signal at 12.17 and 12.03 ppm (low intensity) also revealed that EDM occurs as tautomers, with an enol form as a minor contributor in CDCl_3 solutions (Figure 1). The ^{13}C NMR spectrum (APT) of EDM showed 10 resonances, agree with the proposed structure (see Exper. Part). In the ^{13}C NMR, $\text{C}=\text{O}$ signals were observed at 196.9 (ketone), 162.4 and 166.2 ppm (esters). The signals of two methylene carbons of methacrylate moiety were observed at 135.2 ppm ($\text{CH}_2=\text{C}$) and 126.9 ppm ($\text{CH}_2=\text{C}$). Carbons of OCH_2 groups were appeared at 67.9 ($\text{OCH}_2\text{C}=\text{O}$) and 61.5 (OCH_2CH_3) ppm.

In the IR spectra (Figure 2), characteristic absorption belongs to the $\text{C}=\text{C}$ of the methacrylate unit of EDM at 1637 cm^{-1} , agree the proposed structures of EDM.¹⁶ The intense absorptions cen-

tered at 1752 and 1727 cm^{-1} are assigned to three carbonyl groups from EDM.

Poly(EDM) shows the broad absorption band belongs to $\text{C}=\text{O}$ at 1735 cm^{-1} (Figure 2). The absorption band at 1637 cm^{-1} of the monomer belonging to $\text{C}=\text{C}$ disappeared after the polymerization of EDM. This observation reveals the polymerization of EDM. ^1H and ^{13}C NMR spectra of poly(EDM) could not be recorded due to its very low solubility in organic solvents.

Poly(EDM) shows thermal stability up to 230 °C, as shown in Figure 3. The curves obtained from thermogravimetric analysis have characteristic two-step decomposition regions. The first weight-loss region that appears around 230–320 °C (about 35%) can be related to possible internal eliminations of the ethylene group and CO_2 from the $\text{EtOC}=\text{O}$ unit. Secondary weight loss occurring around 320–520 °C is related to other possible residue eliminations. The glass transition temperature was determined using differential scanning calorimetry (DSC) instruments as 49 °C.

Evaluation of Poly(EDM) as an Adsorbent in SPE; Effect of pH on the Retention of the Trace Metal Ions

To optimize the adsorption conditions for the retention of Mn (II), Co(II), Ni(II), Zn(II) and Pb(II) ions on poly(EDM), the recoveries of the trace metal ions were determined by applying the described procedure by changing the pH of model solutions in the range of 4–9.5 (Figure 4). The recoveries of all the studied metal ions were found to be quantitative ($\geq 95\%$) at pH 8.5. Therefore, pH 8.5 was chosen as the optimum value for further experiments.

Effect of Concentration, Type and Volume of Eluent

The HCl and HNO_3 solutions prepared at various concentrations, between 0.50 and 3.0 mol dm^{-3} , were tested to elute the metal ions retained on the poly(EDM). Quantitative recovery values for Mn (II), Co(II), Ni(II), Zn(II), and Pb(II) ions were obtained with 0.50–3.0 mol dm^{-3} HCl, except for Zn(II) with 3 mol dm^{-3} HCl. The recoveries with 0.50–3.0 mol dm^{-3} HNO_3

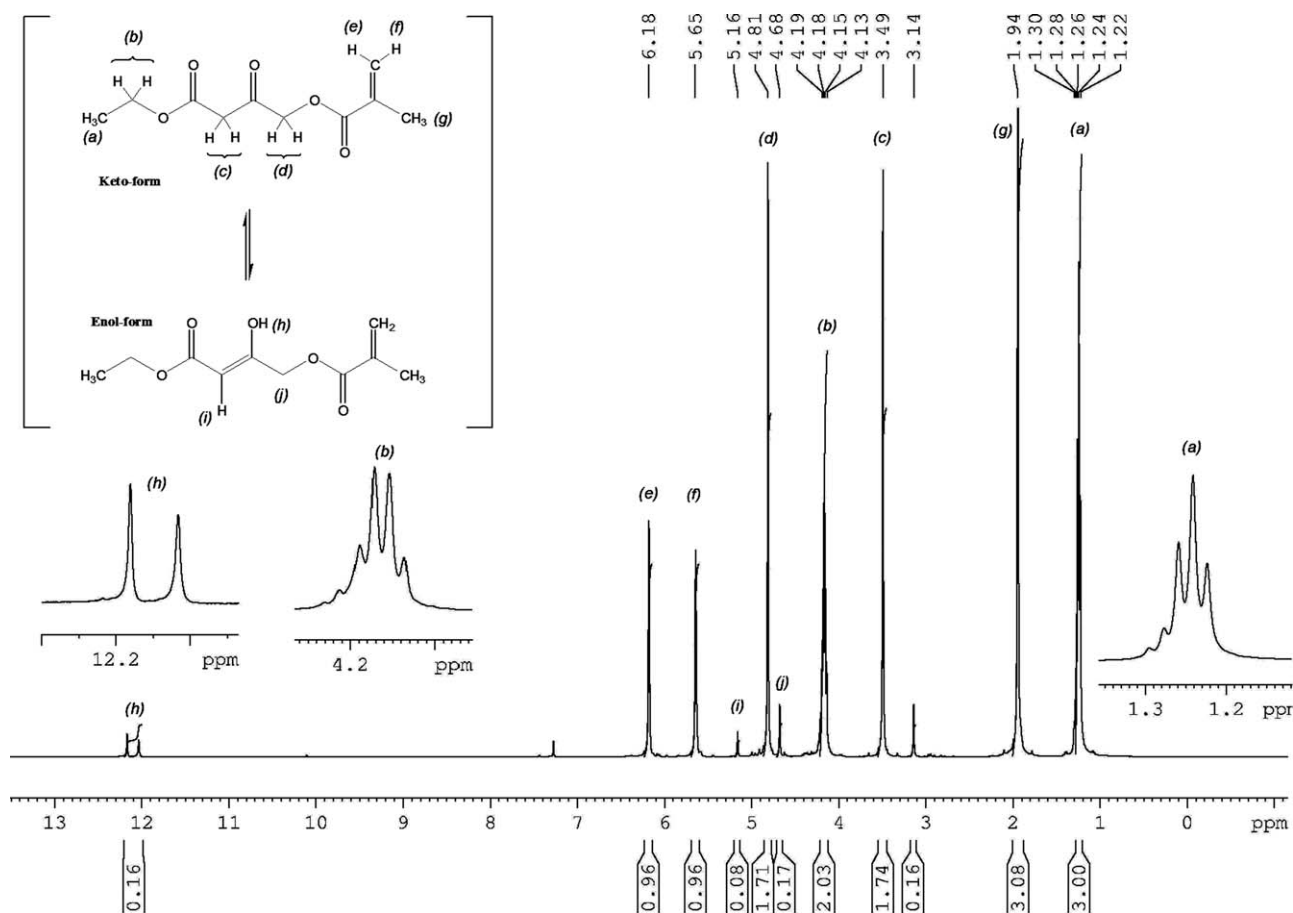


Figure 1. ^1H NMR spectra of EDM in CDCl_3 .

were obtained quantitatively, except for the Zn(II) and Pb(II) with 0.50 and 2.0 mol dm^{-3} HNO_3 solutions, respectively (see Table I). In light of the above observations, 1 mol dm^{-3} HCl

was chosen as the optimal eluent solution. The effect of volume of 1 mol dm^{-3} HCl for the quantitative elution of all the metal ions was also examined in the range of $5\text{--}20 \text{ cm}^{-3}$. The

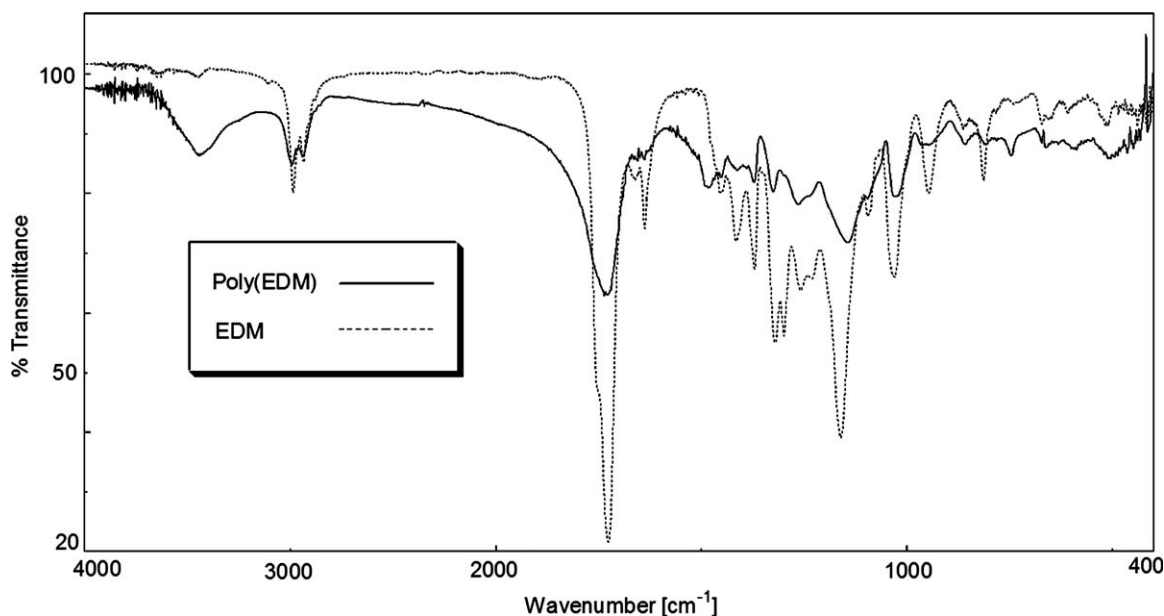


Figure 2. IR spectra of EDM and poly(EDM).

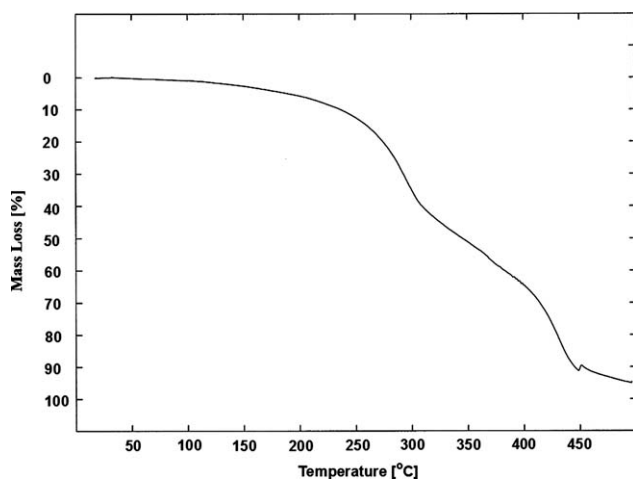


Figure 3. Thermogravimetric analysis curve in N_2 atmosphere of poly(EDM).

recoveries of all the analytes were quantitative for 5 cm^3 of 1 mol dm^{-3} HCl.

Effect of Sample and Eluent Flow Rate

An important parameter affecting recovery and preconcentration time is flow rate. There is a contradiction between recovery and preconcentration time changing with flow rates. Therefore, the effect of sample solution flow rate on analyte recovery was examined under the optimum conditions (pH 8.5, eluent type: 1 mol dm^{-3} HCl, sample volume: 50 cm^3 , solid phase amount: 0.50 g). The sample solution was passed through the column with flow rates ranging from 0.017 to $0.10 \text{ cm}^3 \text{ s}^{-1}$. The recoveries of the metal ions were quantitative up to a flow rate of $0.025 \text{ cm}^3 \text{ s}^{-1}$ for Mn(II), Co(II), Ni(II), Pb(II), and at all the flow rates for Zn(II). Therefore, a flow rate of $0.025 \text{ cm}^3 \text{ s}^{-1}$ was applied for subsequent experiments.

The effect of eluent flow rate on the quantitative elution of the analytes was investigated at flow rates of 0.050 and $0.10 \text{ cm}^3 \text{ s}^{-1}$. The recoveries of the metal ions were quantitative for a flow rate of $0.050 \text{ cm}^3 \text{ s}^{-1}$ for Mn(II), Co(II), Ni(II), and Zn(II) and for all the flow rates for Pb(II). The eluent flow rate of $0.050 \text{ cm}^3 \text{ s}^{-1}$ was chosen as the optimal rate.

Table I. Effect of Type and Concentration of Eluent on the Recovery of the Metal Ions (pH 8.5, Flow Rate of Sample = $0.05 \text{ cm}^3 \text{ s}^{-1}$, Sample Volume = 50 cm^3 , $N = 3$)

Type of eluent and concentration (mol dm^{-3})	Co(II)	Mn(II)	Ni(II)	Pb(II)	Zn(II)
[HCl] = 0.5	98.7 ± 2.3	96.4 ± 3.6	96.2 ± 3.8	98.2 ± 3.0	95.1 ± 6.4
[HNO ₃] = 0.5	100.0 ± 0.0	100.0 ± 0.0	98.5 ± 2.1	97.1 ± 0.0	86.9 ± 4.4
[HCl] = 1.0	100.0 ± 0.0	95.4 ± 7.0	97.3 ± 2.3	97.3 ± 4.6	103.2 ± 1.4
[HNO ₃] = 1.0	98.6 ± 2.5	97.0 ± 1.0	94.7 ± 4.6	100.0 ± 9.1	100.8 ± 7.3
[HCl] = 2.0	97.1 ± 2.5	96.4 ± 0.0	95.0 ± 3.8	98.6 ± 7.9	101.2 ± 5.8
[HNO ₃] = 2.0	96.7 ± 7.4	96.7 ± 7.4	97.6 ± 3.8	90.0 ± 5.2	98.7 ± 4.6
[HCl] = 3.0	101.5 ± 2.5	96.9 ± 4.6	97.3 ± 4.6	97.3 ± 4.6	86.9 ± 2.4
[HNO ₃] = 3.0	98.6 ± 5.0	98.6 ± 5.0	96.9 ± 4.6	97.3 ± 2.3	97.3 ± 4.6

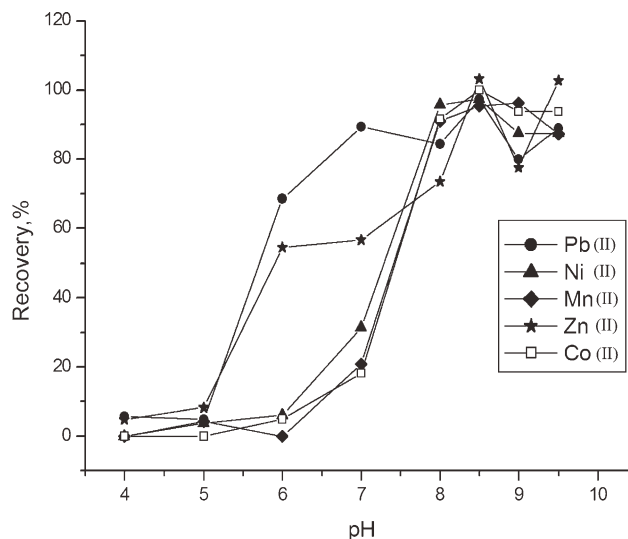


Figure 4. The effect of pH on the recovery of the metal ions (sample volume = 50 cm^3 , eluent = 20 cm^3 of 2 mol dm^{-3} HNO₃, flow rate of sample = $0.025 \text{ cm}^3 \text{ s}^{-1}$, $N = 3$).

Effect of Sample Volume

To determine the maximum sample volume, $5.0 \mu\text{g}$ Mn(II), $10.0 \mu\text{g}$ Co(II), and Ni(II), $2.5 \mu\text{g}$ Zn(II) and $20.0 \mu\text{g}$ Pb(II) were preconcentrated from volumes of 50, 100, 250, 500, and 750 cm^3 of synthetic sample solutions under the optimum conditions by applying the proposed procedure. The recoveries of Ni(II), Zn(II), and Pb(II) were approximately quantitative for up to 500 cm^3 of the sample volume. The breakthrough volumes for Mn(II) and Co(II) were found as 250 cm^3 . Consequently, considering the final solution volume of 5 cm^3 and breakthrough volumes of 500 and 250 cm^3 , enrichment factors of 100-fold for Ni(II), Zn(II), and Pb(II) and 50-fold for Mn(II) and Co(II) were obtained.

Effect of Matrix Ions

The possible influence of matrix ions present in the sea water samples was also examined. The effects of potential interfering ions on the determination of the metal ions were investigated using SSW samples. The results are summarized in Table II. These results show that the proposed preconcentration and

Table II. Effect of Dilution of Synthetic Sea Water on the Recovery of the Metal Ions (pH 8.5, eluent: 10 cm³ of 1 mol dm⁻³ HCl, *N* = 4)

Volume of SSW in 50 cm ³ model solution	Pb(II)	Ni(II)	Mn(II)	Zn(II)	Co(II)
25 cm ³ SSW ^a	61.5 ± 16.3	86.4 ± 0.0	31.3 ± 3.2	100.4 ± 4.3	79.7 ± 4.5
10 cm ³ SSW	65.3 ± 6.1	97.1 ± 3.6	60.8 ± 1.4	96.4 ± 2.9	101.1 ± 2.3
5 cm ³ SSW	59.5 ± 3.6	95.2 ± 1.7	54.3 ± 5.2	95.6 ± 1.0	97.7 ± 4.0
2 cm ³ SSW	69.2 ± 2.1	96.6 ± 0.0	77.1 ± 5.9	94.4 ± 0.9	94.7 ± 0.0
1 cm ³ SSW	97.5 ± 2.1	96.6 ± 1.8	99.0 ± 5.0	99.7 ± 3.5	98.3 ± 4.6

^aDilution was performed with distilled-deionized water.

separation method could be applied to relatively soft water samples, such as lake water.

Analytical Performance of the Method

To assign the detection limit (DL, *n* = 20) of the proposed method, a 50 cm³ portion of blank solution was passed through the column under the optimal experimental conditions and the retained metal ions were eluted. The DLs, obtained at three times the standard deviation of the blank solution by dividing to the slope of the calibration curve, were 3.7 for Mn(II), 3.8 for Co(II), 1.8 for Ni(II), 0.5 for Zn(II), and 6.1 μg dm⁻³ for Pb(II). The precision of the method was determined by performing seven successive retention and elution cycles followed by FAAS. It was found that the recoveries (R% ± *s*) were found to be 100.3 ± 3.4, 100.0 ± 2.6, 95.6 ± 1.4, 100.0 ± 3.5, and 100.8 ± 4.0 for Mn (II), Co(II), Ni(II), Zn(II), and Pb(II), respectively.

Adsorption Isotherm and Adsorption Capacity

The adsorption capacity of poly(EDM) was determined for Co(II) and Ni(II) using the column technique. Therefore, 50 cm³ aliquots of model solutions containing 1–600 mg dm⁻³ Co(II) and Ni(II) from each one at pH 8.5 were passed through the column filled with 0.50 g of the poly(EDM) chelating resin at a flow rate of 0.025 cm³ s⁻¹. The retained metal ions were eluted from the column with 1 mol dm⁻³ HCl. The concentrations of Co(II) and Ni(II) in the eluate were determined by

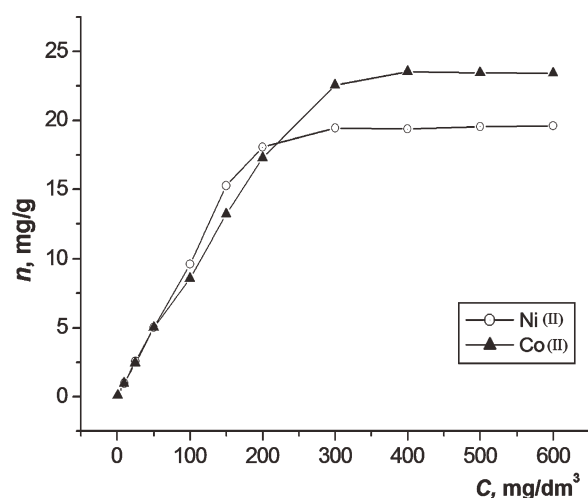


Figure 5. Adsorption isotherms of the chelating resin for cobalt and nickel (pH 8.5, sample volume = 50 cm³, eluent = 5 cm³ of 1 mol dm⁻³ HNO₃, flow rate of sample = 0.025 cm³ s⁻¹, 0.50 g poly(EDM), *N* = 3).

FAAS. The concentration of the adsorbed metal ion (*n*) in mg/g was studied as a function of the metal ion concentration (*C*, mg/dm⁻³) in the initial solution. Figure 5 shows the adsorption isotherms for Co(II) and Ni(II), which conform to the Langmuir equation¹⁷, as *C/n* is proportional to *C*. The adsorption capacities (*n_m*) of the resin for cobalt and nickel were calculated from the Langmuir equation. This equation is given as the following:

$$\frac{C}{n} = \frac{1}{n_m K} + \left(\frac{1}{n_m}\right) C$$

The adsorption capacity (*n_m*) and the binding equilibrium constant (*K*) were calculated from the slope, and the intercept of the regression plot was obtained by the least squares method (Figure 6). The adsorption capacities of the chelating resin for cobalt and nickel were 24.2 mg/g (0.411 mmol/g) and 19.8 mg/g (0.337 mmol/g), and the binding equilibrium constants were 0.057 dm³/mg (3.36 × 10³ dm³/mol) and 0.144 dm³/mg (8.45 × 10³ dm³/mol), respectively. The adsorption capacity of this chelating resin is higher than those of the adsorbents reported in the literature.^{18–20}

Accuracy of the Proposed Method and Application of the Method in SPE

The accuracy of the proposed method was verified by determination of the metal ions in the standard reference materials, namely, TMDA70, TMDA64, and TMDA54.4 fortified lake water

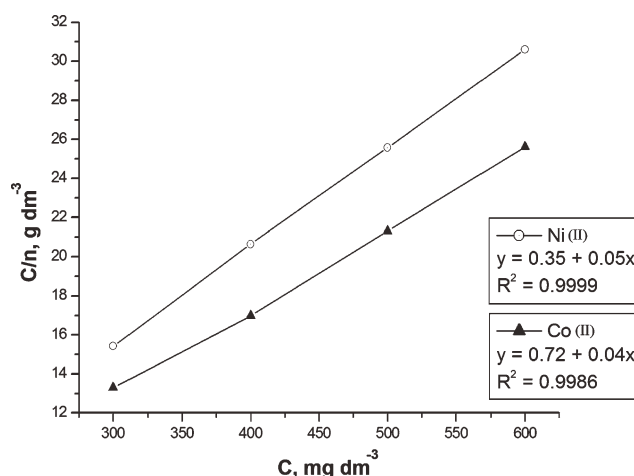


Figure 6. Langmuir isotherms of the chelating resin for cobalt and nickel.

Table III. Determination of the Metal Ions in the Standard Reference Materials by Using the Described Method ($N = 3$)

Analyte		Metal Concentration ($\mu\text{g}/\text{dm}^{-3}$)		
		TMDA70	TMDA64	TMDA54.4
Ni(II)	Certified ^a	328 ± 3	262 ± 2	337 ± 3
	Found ^b	336 ± 7	263 ± 8	329 ± 3
	R (%)	102.4	100.4	97.6
Pb(II)	Certified ^a	443 ± 4	297 ± 2	514 ± 5
	Found ^b	460 ± 4	280 ± 10	507 ± 5
	R (%)	103.8	94.5	98.6
Co(II)	Certified ^a	285 ± 3	270 ± 3	309 ± 3
	Found ^b	293 ± 25	261 ± 3	300 ± 5
	R (%)	102.8	96.7	97.1
Mn(II)	Certified ^a	300 ± 2	299 ± 2	275 ± 2
	Found ^b	292 ± 8	285 ± 3	267 ± 15
	R (%)	97.3	95.3	97.1
Zn(II)	Certified ^a	478 ± 4	313 ^c	537 ± 6
	Found ^b	474 ± 12	313 ± 13	522 ± 10
	R (%)	99.2	100.0	97.2

^aAt 95% confidence level, ^b($\bar{x} \pm s$): Mean ± standard deviation, ^cNot certified.

samples. The results given in Table III show that the described method is in good agreement with the certified values and that the method is applicable for the determination of the analytes in water samples. In addition, the accuracy of the method was tested by performing the recovery studies for waste water sample. Known amounts of the metal ions were added to an aliquot of 200 cm³ of waste water, and the described method was applied to these samples. As shown in Table IV, the recoveries

Table IV. Determination of Metal Ions in 200 cm³ of Waste Water (pH 8.5, Eluent = 5 cm³ of 1 mol dm⁻³ HNO₃, Flow Rate of Sample = 0.025 cm³ s⁻¹, 0.50 g Poly(EDM), $N = 7$)

	Added ($\mu\text{g}/\text{dm}^{-3}$)	Found ($\mu\text{g}/\text{dm}^{-3}$) ^a	R (%)
Ni	-	71.3 ± 2.4	
	100.0	169.5 ± 4.5 ^b	98.2
Co	-	< DL	
	100.0	105.2 ± 3.1	105.2
Zn	-	9.8 ± 0.7	
	25.0	34.1 ± 1.3	97.2
Pb	-	<DL	
	200.0	196.6 ± 5.2	98.3
Mn	-	10.9 ± 1.5	
	50.0	62.2 ± 1.5	102.6

^aEF = 40-fold, ^b($\bar{x} \pm s$): Mean ± standard deviation.

of the analytes were in the range of 97–105% for the waste water. The results indicate that the developed preconcentration method for the Mn(II), Co(II), Ni(II), Zn(II), and Pb(II) was not affected by potential interferences from the major matrix components of the waste water samples.

CONCLUSIONS

We have achieved an efficient process for the synthesis of a chelating monomer (EDM) and poly(EDM) functionalized with β -dicarbonyl moiety starting from readily available reagents. The reaction is simple from an experimental point of view. The monomer and polymer were characterized by spectroscopic methods, and poly(EDM) was investigated for SPE. The poly(-EDM) functionalized with β -dicarbonyl units enriches Mn(II),

Table V. Comparison of Detection Limits (DL, $\mu\text{g}/\text{dm}^{-3}$) and Enrichment Factors (EF) of Some Metal Ions Using the Chelating Resins Functionalized with Chelating Units

Functional group of chelating resin		Co(II)	Mn(II)	Ni(II)	Pb(II)	Zn(II)	Ref.
2,4-Dioxobutyl	DL	3.8	3.7	1.8	6.1	0.5	This Work
	EF	50	50	100	100	100	
1-(2-Pyridylazo)-2-naphthol ^a	DL		0.13	1.2	0.13		[21]
	EF		150	100	100		
Trion ^b	DL		2.5	4.0	24		[22]
	EF		65	150	25		
1,8-Dihydroxy-anthraquinone ^c	DL				0.45	0.71	[7]
	EF				200	200	
1-(2-Thiazolylazo)-2-naphthol ^a	DL		0.39	0.53	1.19		[23]
	EF		50	100	150		
N-(4-Bromophenyl)-2-methacrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid	DL	0.24	0.19	0.37	1.6		[24]
	EF	100	100	100	100		
o-Aminobenzoic acid ^d	DL	6.5		5.0	2.5	2.5	[2]
	EF	150		200	400	400	

^aAnchored on Amberlite XAD-1180, ^bAnchored on Amberlite XAD-2, ^cAnchored on Silica gel, ^dAnchored on Amberlite XAD-4.

Co(II), Ni(II), Zn(II), and Pb(II) ions from the water samples via the SPE method. The method is simple, sensitive, precise, reliable, and accurate. This work indicates that poly(EDM) has potential for the enrichment and separation of analyte ions from water samples as well as for their determinations by FAAS. The results of this work showed that poly(EDM) benefits from good stability in high acidic and basic media. The tolerance limits of interfering ions on the recovery of the analyte ions are quite high. It was also found that the recovery values of the elements after cycles (~ 500) of adsorption and desorption were quantitative. The results acquired from analyses of the standard reference materials (TMDA 54.4, TMDA64, TMDA70 fortified lake water) confirm the reliability of the method. The proposed technique can be applied to environmental samples for the determination of trace amounts of Mn(II), Co(II), Ni(II), Zn(II), and Pb(II).

A comparison of the proposed method with the other preconcentration procedures using various modified adsorbents is given in Table V. The detection limits and enrichment factors of poly(EDM) chelating resin are compatible with other functionalized polymers.

ACKNOWLEDGMENTS

This work was supported by Research Fund of the Erciyes University (FBT-05-10).

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