

Preconcentration and Matrix Elimination for the Determination of Pb(II), Cd(II), Ni(II), and Co(II) by 8-Hydroxyquinoline Anchored Poly(styrene-divinylbenzene) Microbeads

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ABSTRACT: Poly(styrene-divinylbenzene), PS-DVB, microbeads were modified with 8-hydroxyquinoline (8-HQ) following nitration, reduction of $-\text{NO}_2$ to NH_2 , and conversion of NH_2 to diazonium salt. Characterization of pristine, $-\text{NO}_2$, $-\text{NH}_2$, $-\text{N}\equiv\text{N}^+\text{Cl}^-$, and 8-QH functional groups modified microbeads was made by Fourier transform-infrared spectrometry (FTIR) and porosimetry. Total reflectron-X-ray fluorescence spectrometer (TXRF) was used to test the affinity of the 8-HQ modified microbeads to toxic metal ions. 8-HQ-modified microbeads were used to examine the adsorption capacity, recovery, preconcentration, and the matrix elimination efficiency for Pb(II), Cd(II), Ni(II), and Co(II) ions as a function of changing pH, initial metal-ion concentrations, and also equilibrium adsorption time of the

studied metal ions. Preconcentration factors for the studied toxic metal ions were found to be more than 500-fold and recovery between 93.8% and 100.6%. Ultratrace toxic metal-ion concentrations in sea water were determined easily by using modified microbeads. Reference seawater sample was used for the validation of the method, and it was found that recovery, preconcentration, and the matrix elimination were performed perfectly. For the desorption of the toxic metal ions, 3M of HNO_3 was used and desorption ratio shown to be more than 96%. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2714–2722, 2008

Key words: modified PS-DVB; recovery; toxic metals; preconcentration; matrix elimination; TXRF

INTRODUCTION

Heavy metal ions are among the most important contaminants of aqueous samples. Accelerating industrialization causes irreversible metal contamination to aqueous systems.¹ These metal ions are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders.^{2,3} Measurement of the levels of heavy metals has greater importance. Although very sensitive analysis methods and instruments have been developed for their determination, accurate analysis of metals especially at trace level is still one of the most challenging problems of analysts particularly in an area of increasing concern; environmental quality and public health. The levels of metal ions are usually lower than the detection limit of most instruments, and metals usually exist in very complex matrix environments. Direct analysis of metals without a sample preparation technique makes the analysis a cumbersome process due to interferences.^{4–6} Because of these difficulties, a clean-up and preconcentration

step is usually necessary to obtain more reliable data. Many methods including membrane filtration,⁷ coprecipitation,⁸ liquid–liquid extraction,⁹ cloud point extraction,¹⁰ and solid-phase extraction¹¹ have been developed for the preconcentration of heavy metals. Activated carbon,¹² silica gel and chemically bonded silica,^{13,14} zeolites,¹⁵ and polymeric sorbents^{16–18} modified with several chelating groups have been used for the removal and preconcentration of trace metals for many years. Silica-based materials are mostly preferred for chromatographic separations and solid phase extraction applications.^{19,20} Because of the surface hydrophobicity of alkylated silica, the contact of the surface of alkylated silica with predominantly aqueous samples is poor. Unmodified polymeric resins also have a hydrophobic character, and surface contact of these resins is really poor like alkylated silica resins. The surface hydrophobicity of these sorbents usually necessitates a pretreatment step with a polar-activating solvent such as methanol or acetonitrile to obtain better surface contact with aqueous samples. However, the activating solvent can be leached out of the resin, which causes ineffective extraction.²¹ Activated carbon and ion-exchange resins, although being considerably cheap, are generally nonspecific. To

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overcome all these drawbacks, chemically modified resins have been started to use widely. Synthetic polymeric materials have almost entirely displaced inorganic materials for the separation of heavy metal ions because they are easily produced in a variety of compositions and can easily be modified.^{22,23} Poly(styrene-divinylbenzene) and its derivatives are the most preferred polymeric materials used for commercial purposes. Poly(styrene-divinylbenzene)-based sorbents are available under the trade names of Amberlite XAD series and widely studied.^{24–28} Although chemical attachment of different chelating and ion exchanger groups to PS-DVB series resins were also reported,^{21,29} there is still need for PS-DVB-based materials capable of extracting and preconcentrating the metals of interest in both single and competitive media without any loss in the efficiency.

8-HQ is a very good and soft-complexation ligand having great affinity to nearly all metals.^{30,31} The 8-hydroxyquinoline has available complexation sites to metal ions by forming a chelate through the basic nitrogen and phenolic group. Consequently, 8-HQ and derivatives attracted great attention as complexation agents in on-line flow injection systems for the enrichment of metals.^{32,33} The 8-HQ also shows almost no affinity to halogenic anions, which show strong molecular absorption in atomic spectroscopy, hence can be effectively used for the preconcentration of environmental samples. The modification of 8-HQ to different support materials and its metal sorption properties were previously reported by different groups.^{34–40} The ease of modification of PS-DVB microbeads due to aromatic rings and great surface area and power of 8-HQ as a complexing ligand provide new alternatives for the removal and preconcentration of heavy metals.

In this study, a synthetic approach is presented for the modification of poly(styrene-divinylbenzene) microbeads with 8-hydroxyquinoline group to increase their capability for retention of metals even at very low concentrations. Modified microbeads were characterized by FTIR spectrometry and mercury intrusion porosimeter. The effects of pH, concentration, and equilibration time were tested over artificial and environmental samples.

EXPERIMENTAL

Chemicals

PS-DVB (12% w/w DVB) microbeads having an average of 8 μm diameter were purchased from Aldrich (Milwaukee, USA). To obtain 90% HNO_3 by weight, the mixture $\text{HNO}_3/\text{H}_2\text{SO}_4$ in 50% v/v was distilled up to 95% and then diluted to 90%. Lead nitrate ($\text{Pb}(\text{NO}_3)_2$) was purchased from BDH, England.

Cadmium nitrate ($\text{Cd}(\text{NO}_3)_2$), nickel nitrate ($\text{Ni}(\text{NO}_3)_2$), cobalt nitrate ($\text{Co}(\text{NO}_3)_2$), and spectroscopic grade potassium bromide for FTIR were obtained from Merck (Darmstadt, Germany) and used without further purification. 8-Hydroxyquinoline was purchased from Aldrich (Buchs, Switzerland). A mixture of all the metal ions was prepared by using deionized water of $18.2 \text{ M}\Omega \text{ cm}^{-1}$ resistivity obtained from a Milli Q-water purification system (Millipore, Bedford, MA). All solutions were prepared and used freshly.

Apparatus

Atomic absorption spectrometer

A PerkinElmer Analyst 100 Atomic Absorption spectrometer with HGA 800 Electrothermal Atomization unit (GF-AAS, Boston, MA), equipped with deuterium lamp back-ground correction was employed. Hollow cathode lamp of lead, cadmium, nickel (PHOTRON, Victoria, Australia), and cobalt (Perkin Elmer, Shelton, USA) were used. Pyrolytic-coated graphite furnaces (PerkinElmer, Boston, MA) were used for analyses with the direct atomization from the wall of pyrolytic-coated graphite furnace.

Total reflection-X-ray fluorescence spectrometer

Total reflection X-ray fluorescence spectrometry (TXRF) measurements were performed using an EXTRA IIA total reflection X-ray fluorescence spectrometer (ATOMIKA Instruments GmbH, Oberschleißheim, Germany). The operating conditions of the TXRF spectrometer were the following: power: Mo anode X-ray tube (50 keV, 38 mA), cut-off filter, Si(Li) detector with a surface area of 80 mm^2 ; resolution: 168 eV, interaction time 500 s. Germanium was used as an internal standard for the experiments. Hundred microliters of metal-ion solutions were spiked with standard solution of germanium to give a final concentration of 4 mg cm^{-3} in the samples. From these spiked samples, 25 μL was deposited onto a quartz carrier and then dried for 30 min in a clean box. Each sample was analyzed making three replicates.

METHODS

Modification of PS-DVB microbeads with $-\text{NH}_2$ group

PS-DVB microbeads were first nitrated through a typical nitration reaction, described below to modify the polymeric microbeads further with $-\text{NH}_2$ groups. PS-DVB beads (1 g) were added into 4 mL of 90% HNO_3 in small portions. Because the nitration reaction was extremely exothermic, reaction

mixture was kept at 0°C in an ice bath during the reaction. After finishing the addition of the microbeads, reaction mixture was kept at 25°C for 1 h. Then, the microbeads were filtered and washed with cold water several times to remove any unreacted HNO₃. Finally, microbeads were washed with acetone and dried in a vacuum oven at 60°C. Nitration yield was determined gravimetrically, and 42 wt % increment was found when compared with the initial weight of the beads. The weight increment agrees well with the theoretical calculation based on complete nitration all aromatic rings. For the conversion of —NO₂ to —NH₂, a reduction reaction was carried out. For this purpose, 1 g of nitrated microbeads was refluxed in the presence of HCl by adding tin filings in small portions at 80°C. To check full conversion of —NO₂ to —NH₂, FTIR spectra of the samples were recorded after each addition of tin filings. It was found that 2.8-g tin filings and 5-mL concentrated HCl were required to reach complete reduction. After the completion of the reduction reaction, an additional 5-mL HCl was added for the oxidation of remaining tin filings, and then the reaction mixture was cooled to room temperature. Microbeads were filtered and washed with 1M HCl, 1M NaOH, and water, respectively. Finally, microbeads modified with —NH₂ functional groups were dried in vacuum oven at 60°C.

Modification of the PS-DVB microbeads with 8-hydroxyquinolinone functional groups

For the modification of PS-DVB microbeads with 8-HQ groups, microbeads modified with NH₂ groups described earlier were used. Amino groups were converted to diazonium chloride salts as the first step for the modification of PS-DVB by 8-HQ. NH₂-modified microbeads (1 g) were added to a solution containing 3-mL concentrated HCl and 6-mL water in a flask. Cooled NaNO₂ solution (0.63 g of NaNO₂ in 2 mL water) was added to the polymeric suspended mixture at 0°C drop by drop. The reaction temperature was kept at 0°C using an ice bath. After NaNO₂ addition was completed, reaction mixture was still kept at 0°C for an additional 1 h period. Then aryl diazonium chloride reactive group carrying microbeads were filtered off and washed with cold water. Because the diazonium chloride salts were not very stable, these microbeads were subjected to coupling reaction immediately after the synthesis. Aryl diazonium salts carrying microbeads (1 g) were added to the solution of 8-HQ solutions (0.57 g in 5 mL acetone/water mixture 1 : 1 v/v) for coupling reaction at 0°C. The color change from light brown to dark was observed during the coupling reaction. The mixture was kept overnight at 25°C to reach complete conversion. Finally, microbeads were

washed with water and acetone and then dried in vacuum oven at 60°C. The weight of 8-HQ-modified microbeads, obtained finally from 1 g of initial aryl diazonium salts carrying microbeads, was weighted and found to be 1.57-g-modified microbeads. 8-HQ content of 8-HQ-modified microbeads was calculated 0.330 g or 2.28 mmol 8-HQ for 1-g 8-HQ-modified microbeads.

Characterization of modified microbeads

FTIR spectra of pristine and modified PS-DVB microbeads were recorded by using FTIR spectrometer (Nicolet, 520 Model FTIR Spectrometer, USA). A few milligrams of sample were thoroughly mixed with 0.1 g of KBr, pressed into pellet form, and the spectrum was recorded. For the measurements of BET surface area, pore size and pore volume of the plain and modified microbeads Quantachrome, NOVA 2000 series volumetric gas adsorption instrument was used.

Batch-wise adsorption of toxic metal ions onto 8-HQ-modified PS-DVB microbeads

Toxic metal-ion adsorption from single metal-ion aqueous solutions was investigated via batch-wise adsorption experiments. Effects of the initial concentration, the adsorption isotherms, and pH of the medium on the toxic metal-ion uptake were studied. About 10 mg L⁻¹ of 50 mL of single-toxic metal-ion solutions were treated with 0.05 g of polymeric material for 24 h in a flask stirred magnetically at 300 rpm at different pH values in the 0.5–8.0 pH interval adjusted with HNO₃ and NaOH at 25°C. For the toxic metal-ion uptake from single solution, 50 mL of aqueous metal-ion solution with different concentrations (1–800 mg L⁻¹) were treated for 12 h at room temperature with 0.05 g of ligand-modified PS-DVB at pH = 6.0. After the predetermined equilibrium adsorption time, the polymeric microbeads were removed from the adsorption medium, and concentration of the toxic metal ions in the aqueous phase was measured by a GF-AAS. The amount of adsorbed toxic metal ions onto the modified microbeads was obtained by using the following expression.

$$q = [(C_o - C_A)V]/m$$

where q is the amount of the toxic metal ion adsorbed (mg/g polymer) onto the polymer, C_o and C_A are the concentrations of the toxic metal ions initially and after reacting absorption equilibrium, respectively (ppm). V is the volume of the aqueous phase (mL), and m is the amount of the polymer (g).

To find the equilibrium-adsorption time of the toxic metal ions, 50 mL of 100 mg L⁻¹ toxic metal-ion solutions were treated with 0.05 g of modified polymer at pH = 6.0 for 72 h. During the course of the experiment, 100 μ L samples were taken out and toxic metal-ion concentrations were measured by GF-AAS, and then equilibrium adsorption time of the toxic metal ions was determined.

Regeneration of polymeric microbeads

The regeneration of polymeric microbeads after the adsorption of metal ions was examined using 3.0M of HNO₃ to determine the regeneration of the modified PS-DVB microbeads for toxic metal ions. Toxic metal ion adsorbed polymeric beads were placed in desorption medium and stirred at 500 rpm for 5 h at 25°C. The metal-ion concentration released from polymeric materials into the aqueous phase was measured by GF-AAS. Desorption ratio was calculated from the amount of metal ion initially taken up by the polymeric material, and the final metal-ion concentration in the desorption medium.

Recovery of toxic metal ions

Fifty milliliters of 10 mg L⁻¹ of each toxic metal ion such as Pb(II), Cd(II), Ni(II), and Co(II) in the same mixture was treated with 0.05 g of modified polymer. After the treatment of the solution with polymeric microbeads, toxic metal-ion-loaded microbeads were placed into the desorption medium containing 50 mL of 3.0M HNO₃. Toxic metal-ion concentrations in the desorption media were measured GF-AAS. From the initial and final concentration, recovery for each toxic metal ion was calculated.

Preconcentration of toxic metal ions

For the preconcentration of metal ions, 1 L solution of mixed metal ions each at 0.02 μ g L⁻¹ concentrations was treated with 0.05 g of polymeric microbeads. After 12 h of adsorption time, supernatant was separated and metal-ion adsorbed modified microbeads were placed in 2 mL of 3M HNO₃ for the desorption of toxic metal ions from polymeric microbeads for 5 h and then metal-ion content in desorption medium was analyzed by GF-AAS. Using the initial and final metal-ion concentrations, preconcentration factors of the metal ions were calculated.

Method validation

Two fifty milliliters of BCR CRM 403 sea-water (Community Bureau of Reference) reference sample solution containing 0.175, 3.9, 103, 4.4, 0.117, and 25.7 nmol kg⁻¹ of Cd(II), Cu(II), Mo(II), Ni(II), Pb(II),

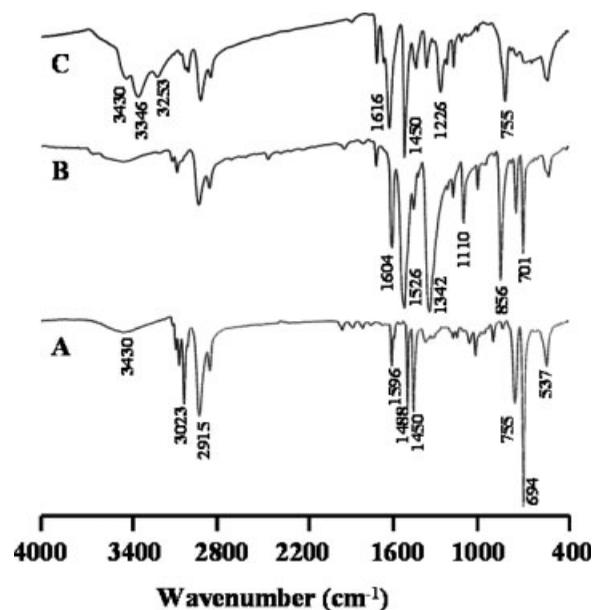


Figure 1 FTIR spectra of (A) PS-DVB, (B) PS-DVB after attaching NO₂ groups, and (C) PS-DVB after reducing NO₂ groups to NH₂ groups.

and Zn(II) metal ions were treated with 0.05 g of 8-HQ-modified PS-DVB microbeads after adjusting to pH = 6.0 to validate the method. After the adsorption equilibrium time, which was 5 h, polymeric microbeads were separated from adsorption medium by centrifugation (3000 rpm for 10 min) and metal ions desorbed in 2 mL of HNO₃ solution for 5 h at room temperature. Finally, metal-ion concentrations in the desorption medium were measured by Inductively Coupled Plasma-Mass Spectrometry equipped with AS-510 autosampler (ICP-MS, 7500a series, Agilent, UK). Argon plasma was used and flow rate of all gases were set at 15.0, 0.90, and 1.11 L min⁻¹ for coolant, auxiliary, and nebuliser gases. Uptake rate of the sample was set to 1.0 mL min⁻¹, spray chamber was cooled by water, scan acquisition mode was set, and pulse counting detector was used with 320 μ s/channel Dwell time.

RESULTS AND DISCUSSION

Characteristics of pristine and modified PS-DVB microbeads

Characterization by FTIR

For the characterization of the pristine³ NO₂ and NH₂-modified PS-DVB microbeads, FTIR spectra were recorded and given in Figure 1. The absorption bands at 1526 and 1342 cm⁻¹ in Figure 1(B) were assigned to the asymmetric and symmetric —N—O stretching vibrations, respectively. The absorption band observed at 856 cm⁻¹ was assigned to the —C—N stretching vibration that characterizes the

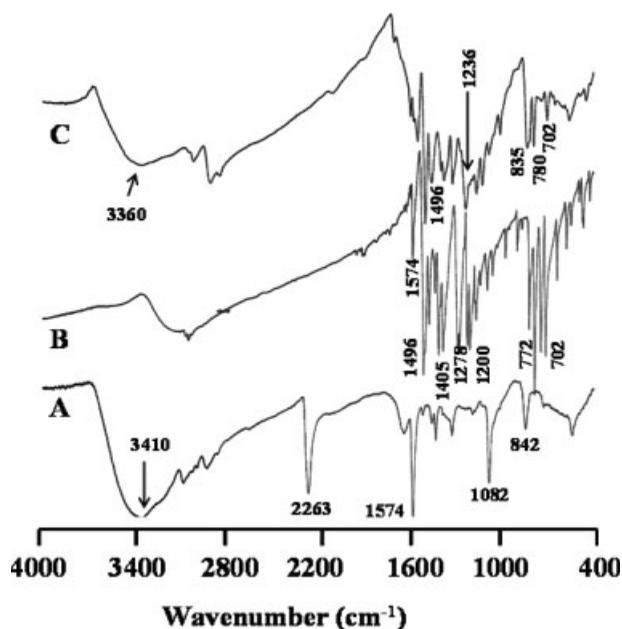


Figure 2 FTIR spectra of (A) PS-DVB modified with diazonium salt, (B) 8-hydroxyquinoline, and (C) PS-DVB after modification with 8-hydroxyquinoline.

attachment of $-\text{NO}_2$ groups to the aromatic carbons of pristine polymeric microbeads. These results indicated that the successful attachment of $-\text{NO}_2$ groups to the PS-DVB microbeads was achieved. After the nitration of the PS-DVB microbeads, weight of pristine polymer was increased by 42%. This result showed that high amount of $-\text{NO}_2$ groups was loaded onto the polymeric microbeads. The main spectral changes on the FTIR spectrum of nitrated PS-DVB, when the reduction reaction was carried out, were the disappearance of $-\text{N}\cdots\text{O}$ stretching vibration bands at 1526 and 1342 cm^{-1} . The new absorption band at 1616 cm^{-1} was assigned to the $-\text{N}-\text{H}$ bending vibration. The most striking indication of the reduction of $-\text{NO}_2$ groups to the $-\text{NH}_2$ groups was the appearance of new absorption bands at 3253 and 3430 cm^{-1} , which were attributed to the $\text{N}-\text{H}$ stretching vibrations [Fig. 1(C)]. FTIR spectra of $-\text{N}\equiv\text{N}^+\text{Cl}^-$ modified PS-DVB were shown in Figure 2(A), that of 8-HQ in Figure 2(B), and 8-HQ-modified PS-DVB in Figure 2(C). The band at 1616 cm^{-1} , which was the characteristic absorption band of the $\text{N}-\text{H}$ bending, disappeared after formation of the diazonium salt.⁴¹ The absorption band at 2263 cm^{-1} was assigned to the $\text{N}\equiv\text{N}$ stretching vibration of diazonium chloride salt.⁴¹ Also, new absorption band appearing at 1082 cm^{-1} confirms the formation of the diazonium salt [Fig. 2(A)].

The absorption band at 2263 cm^{-1} attributed to the $\text{N}\equiv\text{N}$ stretching vibration diminished dramatically and disappeared upon modification with 8-HQ. This showed that the diazonium salt was modified

with 8-HQ to yield the 8-HQ-modified microbeads and some diazonium salt moieties were converted to $-\text{OH}$ groups. The intense absorption band at 1082 cm^{-1} also disappeared. These two spectral changes pointed out that the chemical attachment of 8-HQ groups was successfully made onto PS-DVB microbeads. FTIR spectra of the 8-HQ-modified microbeads showed similar absorption peaks with the adsorption peaks of 8-HQ at almost the same wavenumbers of 702, 780, 1405, and 1496 cm^{-1} [Fig. 2(C)].

Pore size analysis

Figure 3 shows mercury intrusion porosimetry results for pristine and 8-HQ-modified microbeads. According to these results, the pore size of pristine microbeads varied between 20 and 1000 Å. The plot also shows that the pristine microbeads contain only micropores. Chemical introduction of 8-HQ functional groups to the polymer backbone resulted with the coverage of pores. Disappearance of micropores and formation of meso- and macropores can be interpreted as the successful attachment of functional groups. Specific surface areas were found to be 85.83 $\text{m}^2 \text{g}^{-1}$ for pristine and 2.91 $\text{m}^2 \text{g}^{-1}$ for 8-HQ-modified PS-DVB, respectively. Alteration of specific surface area also indicates a surface modification.

ADSORPTION/DESORPTION

Metal-ion adsorption onto 8-HQ-modified PS-DVB microbeads

pH effect

pH is the main parameter for the metal-ion adsorption onto the complexation ligand-modified poly-

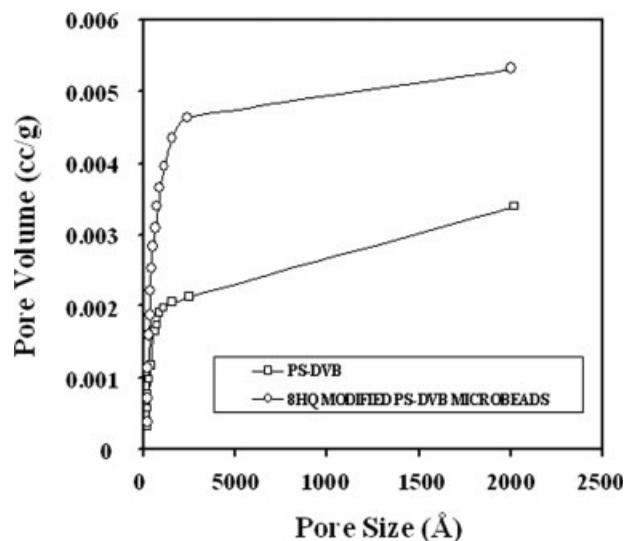


Figure 3 Pore size and pore volume changes of plain and 8-hydroxyquinoline-modified PS-DVB microbeads.

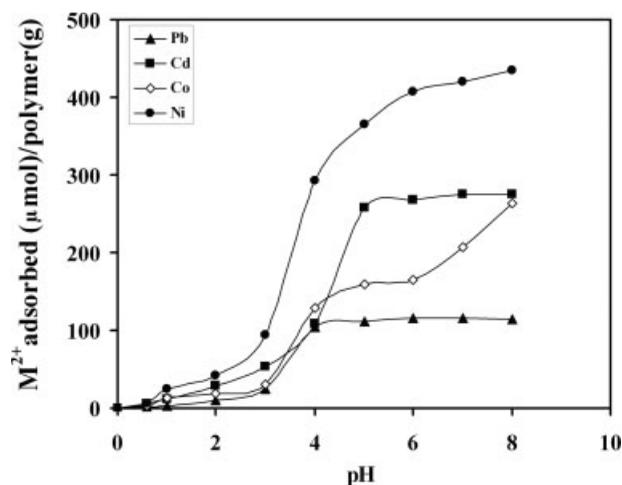


Figure 4 pH effect on the metal ion adsorption of 8-HQ-modified PS-DVB microbeads. Initial metal ion concentration: 10 mg L^{-1} ; temperature: 25°C ; amount of polymer: 0.020 g ; volume of the solution: 50 mL .

meric sorbents. Mainly, at low pH values, the metal-ion ligand complexes are unstable because of the protonation of some functional groups on the complexation ligands. Also, at low pHs, removals of toxic metal ions from some aqueous medium are not feasible due to the consumption of high amount of acidic reagents. pH effect for the toxic metal-ion adsorption onto the 8-HQ-modified PS-DVB microbeads was studied at different pH values between 0.5 and 8.0 from the single metal-ion solutions. The pH dependence of toxic metal-ion adsorption onto the ligand-modified polymeric microbeads is shown in Figure 4. Up to $\text{pH} = 5.0$, Pb(II) and Cd(II) showed the same behavior and adsorption capacity of microbeads for these ions increased and then reached equilibrium adsorption values. After $\text{pH} = 5.0$, Ni(II) and Co(II) ions showed different adsorption behavior and adsorption of Ni(II) continued to increase up to $\text{pH} = 7.0$ reaching a plateau. This behavior can be explained as due to double-layer formation, protonation of the functional groups, hydrolysis metal ions at low pH and produce different hydrolysis forms and causes the adsorption capacity of the metal ions and diffusion type of adsorption of Ni(II). In the case of Co(II), pH-dependent adsorption behavior is different from the other toxic metal ions namely Pb(II), Cd(II), and Ni(II). Up to $\text{pH} = 4.0$, adsorption increased rapidly and reached first equilibrium value until $\text{pH} = 6.0$. At pHs higher than 6.0, adsorption of Co(II) started to increase again until $\text{pH} = 8.0$. This shows that Co(II) adsorption shows the same behavior as Ni(II) showed. The adsorption capacities of the studied ions were found to be 445, 267, 262, and $104 \text{ }\mu\text{mol}$ for Ni(II), Cd(II), Co(II), and Pb(II) at $\text{pH} = 8.0$ in the 10 mg L^{-1} initial metal-ion solutions, respectively.

Initial concentration effect

The adsorption capacity of the studied toxic metal ions onto 8-HQ-modified polymer was examined using different initial concentrations of metal-ion solutions at $\text{pH} = 6.0$ in single and competitive metal-ion medium, and the results are given in Figure 5. In the case of competitive medium, up to 100 mg L^{-1} initial metal-ion concentrations, adsorption values increased very rapidly and reached adsorption equilibrium value at 250 mg L^{-1} for Co(II) and Ni(II) and 500 mg L^{-1} for Pb(II) and Cd(II) ions [Fig. 5(A)]. The reason for high-initial metal-ion concentrations observed for Pb(II) and Cd(II) compared to Ni(II) and Co(II) maybe due to the diffusional drag of Pb(II) and Cd(II) resulting from their high hydrated ion radius compared to Ni(II) and Co(II) in the aqueous medium. The adsorption capacities of the microbeads of the metal ions were found to be 6.7, 5.3, 3.5, and 0.8 mmol g^{-1} polymers for Co(II), Ni(II), Pb(II), and Cd(II), respectively, in the

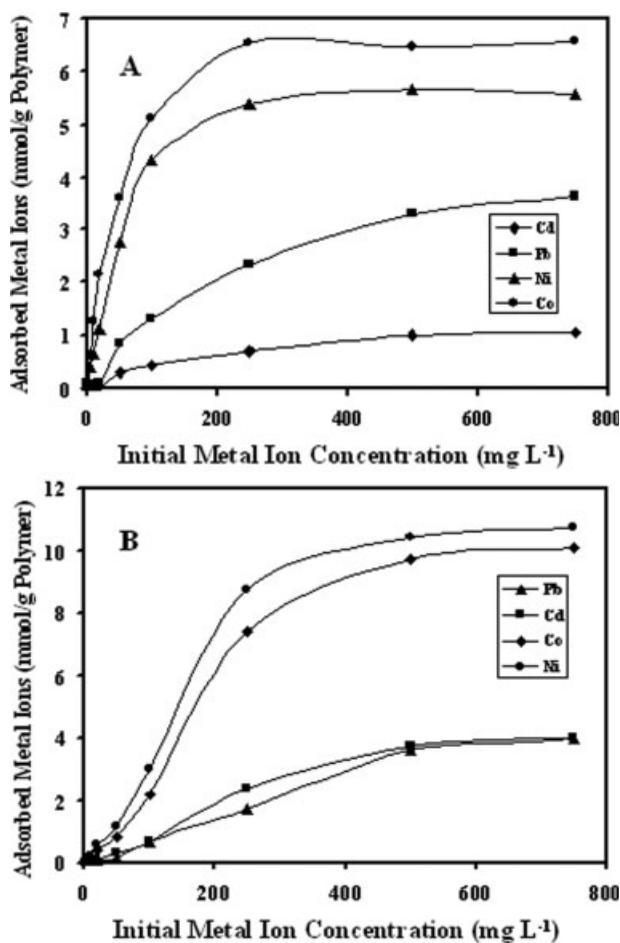


Figure 5 Adsorption capacities of metal ions onto the 8-HQ-modified PS-DVB microbeads. (A) In competitive medium and (B) in non-competitive medium. $\text{pH} = 6.0$; temperature: 25°C ; amount of polymer: 0.020 g ; volume of the solution: 50 mL .

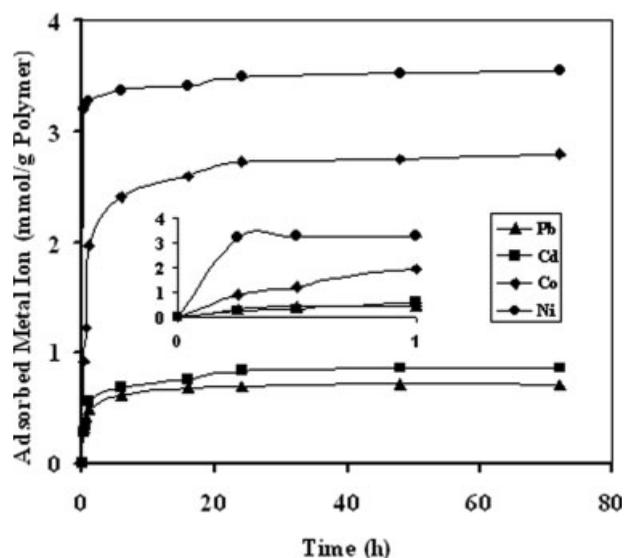


Figure 6 Adsorption isotherms for the metal ions onto 8-HQ-modified PS-DVB microbeads. Initial metal ion concentration: 100 mg L^{-1} ; pH: 6.0; temperature: 25°C ; amount of polymer: 0.020 g ; volume of the solution: 50 mL .

competitive medium. In noncompetitive (in the single-ion medium) case, equilibrium adsorption values were attained at 500 mg L^{-1} for all studied metal ions, and the adsorption capacities for the metal ions were not changed critically compared to the results obtained in competitive medium [Fig. 5(B)]. In noncompetitive media, adsorption capacities of the microbeads for the metal ions were found to be 10.6 , 9.9 , 3.8 , and 3.9 mmol g^{-1} polymers for Co(II) , Ni(II) , Pb(II) , and Cd(II) respectively. In the noncompetitive medium, adsorption capacity increment of cadmium ion was increased about fourfold with respect to competitive case. For others, the adsorption capacity increments were not found to be significantly different. These results showed that the cadmium ion is competing with the Co(II) and Ni(II) ions, but the affinity of the Co(II) and Ni(II) were higher than the affinity of cadmium ions to 8-HQ on the PS-DVB microbeads.

Adsorption isotherms

For the feasible removal, recovery, and preconcentration of the metal ions from different aqueous media, the adsorption time should be short enough both for laboratory tests and industrial applications. Hence adsorption isotherms of the toxic metal ions onto the 8-HQ-modified PS-DVB microbeads was examined at 100 mg L^{-1} metal-ion solutions at $\text{pH} = 6.0$, and the results are given in Figure 6. Between 0 and 45 min, adsorption value increased very rapidly almost reaching the equilibrium adsorption value in the first hour for all studied metal ions. Because the adsorp-

tion capacity changes were not observed to be more than 5% for all metal ions from 1 to 24 h, one hour of adsorption time onto the polymeric sorbents can be considered to be short and feasible for the metal-ion adsorption processes in large scale.

Recovery and preconcentration of toxic metal ions

For the recovery and preconcentration of the toxic metal ions, first of all suitable desorption agents were tried to be found for the desorption of the toxic heavy metal ions from the PS-DVB microbeads. About 3.0 M HNO_3 was found to be the optimum agent, because the desorption ratio of all toxic metal ions were higher than 96%. Therefore, 3.0 M HNO_3 was chosen as desorption agent for the studied metal ions. In this study, 5 h desorption times were used for all desorption experiments. To examine the different desorption times, 1 and 3 h desorption times were also tested, and minimum 92.5% and 95.7% desorption ratios were obtained for these times for all studied metal ions. No considerable recovery improvement was observed when maximum desorption ratio was reached at 72 h desorption time. About 100 mg L^{-1} 50 mL of each single metal-ion solutions were treated with ligand-modified polymer and then metal-ion adsorbed polymeric sorbents transferred into $50\text{-mL } 3.0 \text{ M HNO}_3$ solution. All adsorbed toxic metal ions were desorbed into the desorption media, and the released metal ions were measured by GF-AAS. From the theoretical and experimental results, recovery was calculated and found to be 97.2, 98.6, 96.8, and 96.2% for Co(II) , Ni(II) , Cd(II) , and Pb(II) , respectively. These results showed that the recoveries of the toxic metal ions are satisfactory from aqueous media when the 8-HQ-modified PS-DVB microbeads were used. For the preconcentration of the metal ions, 0.5 L of $0.02 \text{ } \mu\text{g L}^{-1}$ of each single metal-ion solutions were treated with ligand-modified polymeric microbeads and desorbed into 2 mL of desorption agent as described in the recovery experiments. Finally, it was found that for all studied metal ions preconcentration factors were at least 500-fold. This would allow parts per trillion detection limits to be reached for the toxic metal ions in aqueous solutions. After the preconcentration experiments, recoveries of the toxic metal ions were found to be 97.4, 100.6, 95.8, and 93.8 % for Co(II) , Ni(II) , Cd(II) , and Pb(II) , respectively.

Method validation

To test the validation of the method used in this study, 250 mL of BCR CRM 403 sea-water reference solution containing 0.175 , 3.9 , 103 , 4.4 , 0.117 , and $25.7 \text{ nmol kg}^{-1}$ of Cd(II) , Cu(II) , Mo(II) , Ni(II) , Pb(II) ,

TABLE I
Method Validation Results

Metal ions	Metal ion concentrations (nmol kg ⁻¹)		% Recovery
	Certified value	Found	
Cd(II)	0.175	0.178 ± 0.007	101.7 ± 0.6
Cu(II)	3.9	3.6 ± 0.2	92.3 ± 1.4
Mo(II)	103	104 ± 0.6	100.9 ± 0.9
Ni(II)	4.4	4.3 ± 0.02	97.7 ± 0.3
Pb(II)	0.117	0.115 ± 0.005	98.3 ± 1.4
Zn(II)	25.7	25.8 ± 0.1	100.4 ± 1.1

Reference material: sea-water (BCR CRM 403).⁴²

n = 5 with 95% confidence.

ICP-MS was used for the determination of metal ions.

and Zn(II) metal ions were treated with 0.05 g of 8-HQ-modified PS-DVB microbeads after adjusting the solution to pH = 7.0 with NaOH. After the adsorption equilibrium time, which was 5 h, polymeric microbeads were separated from adsorption medium and desorbed into 2 mL of 3.0M of HNO₃ solution for 5 h at room temperature. Finally, metal-ion concentrations in desorption medium were measured by ICP-MS, and the results are given in Table I. It can be seen from Table I that recovery of these metal ions was higher than 92.3% and close to 100% for most metal ions studied, and the method could be used very reliably and efficiently for the recovery of metal ions from sea water by eliminations the matrix effects from the analyzing samples despite the toxic metal-ion concentrations were very low.

TXRF studies for toxic metal ions

To follow adsorption of the metal ions onto 8-HQ-modified PS-DVB microbeads and the desorbed metal ions, an actual sea-water sample collected from Izmir gulf-Aegean Sea-Turkey. The metal-ion concentrations in the sea-water sample could not be determined using TXRF technique because of the high amount of matrix elements and also the high concentration of the salts. High-salt concentration prevented the formation of homogeneous and suitable sample thickness on the TXRF sample holder. Therefore, TXRF spectrum could not be obtained for this sample. The adsorption-desorption cycle was applied onto 8-HQ-modified PS-DVB microbeads, and the desorbed solution to take TXRF spectrum, which is given in Figure 7(A). All the toxic metal ions, Fe, Cu, Zn, and Pb were followed easily and other alkaline and earth alkaline metal ions such as K, Ca, Rb, and Sr were also recovered in high concentrations. From these results, the concentration of Fe, Cu, Zn, and Pb were found to be 0.83, 0.12, 0.77, and 0.02 mg L⁻¹. For the standard mixture that was prepared using 1 mg L⁻¹ each metal ion in the

solution, TXRF spectra were taken by using the standard solution after the adsorption and also after the desorption, and the normalized peak intensity results are given in Figure 7(B,C). It was observed that the concentration of the metal ions decreased almost by 90% compared to initial concentrations and also desorbed metal-ion concentrations were found to increased about 90% showing efficient adsorption-desorption cycle for the studied metal ions. The TXRF results showed that the aqueous samples containing high amount of salts therefore

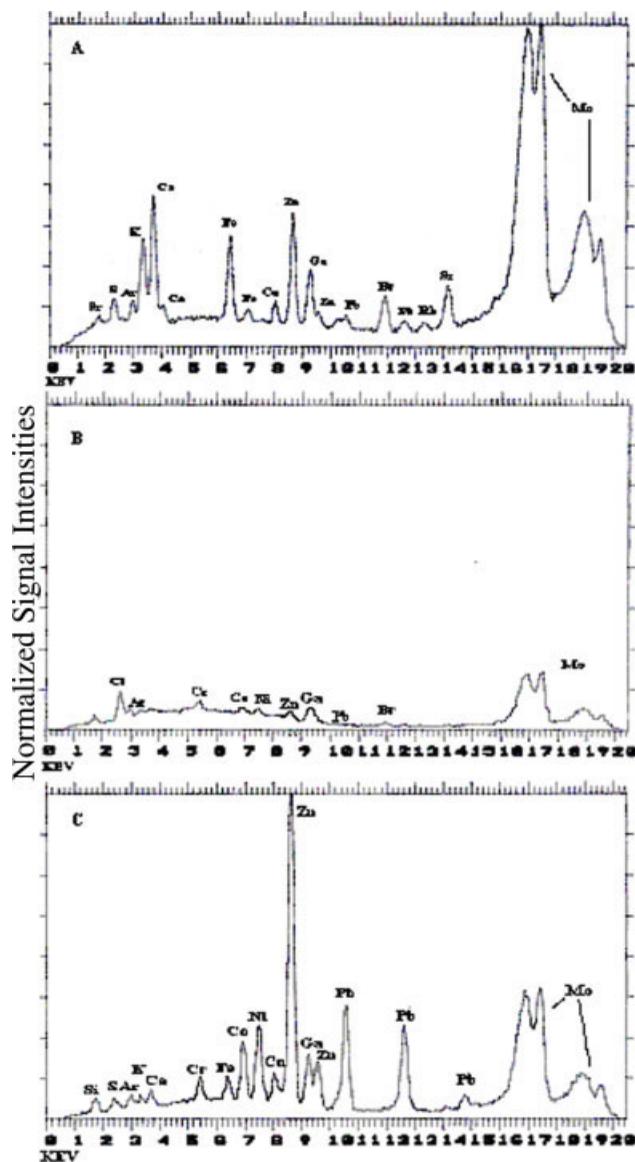


Figure 7 TXRF spectra of (A) sea water after adsorption and desorption on 8-HQ-modified PS-DVB microbeads; (B) artificial mixture after adsorption; and (C) artificial mixture after desorption. Artificial mixture contains 10.0 mg L⁻¹ Zn(II) and 1.0 mg L⁻¹ containing Co(II), Cu(II), Ni(II), Cr(III), Pb(II), and Fe(III). Gallium was used as internal standard. Molybdenum X-ray tube was used as X-ray source.

complicating the sample preparation for TXRF due to the thickness of the dried sample on the sample holder could be analyzed easily when the method described in this study was used. For other aqueous samples, method could be used efficiently, and pre-concentrated samples could be analyzed by TXRF at trace amounts of the metal ions in aqueous samples down to sub-microgram per liter concentrations.

CONCLUSION

It is shown that the PS-DVB microbeads could be modified chemically with 8-hydroxyquinoline ligand specific to Pb(II), Cd(II), Co(II), and Ni(II) toxic metal ions. Matrix elimination from the aqueous samples using ligand-modified polymeric microbeads in the analyses of Pb(II), Cd(II), Co(III), and Ni(II) was perfectly achieved. Validation of method developed was performed by using reference sea-water standard, and it was found that the method worked very efficiently for the recovery and preconcentration of heavy metal ions in sea-water samples. It was found that the same microbeads could be used repeatedly for the recovery, preconcentration, and also matrix elimination experiments due to the high-desorption ratios. TXRF spectrometer was used to test the efficiency of the method developed by using standard toxic metal-ion mixture both after the adsorption and the desorption experiments and for sea-water sample eliminating the salt effect. TXRF results showed that matrix elimination and preconcentration might be possible on the 8-HQ-modified PS-DVB microbeads.

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