Synthesis, characterization and application of a chelating resin for solid phase extraction of some trace metal ions from water, sediment and tea samples

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ARTICLE INFO

ABSTRACT

A new chelating resin, poly (2-thiozylmethacrylamide-co-divinylbenzene -co-2-acrylamido-2-methyl-1-propanesulfonic acid) was successfully prepared in the present work. Its composition, morphology, and properties were studied by Fourier transform infrared spectroscopy, scanning electron microscopy, elemental analysis, and thermogravimetric analysis. Several factors affecting the extraction of the metal ions including pH, the eluent type and concentration, flow rate, sample volume, and effect of interfering ions were investigated. The adsorption capacity of the resin for the elements studied was found in the range of 4.76–13.0 mg g^{-1}. A preconcentration factor of 150 was achieved at the optimum conditions. The limits of detection (3s/b) varied from 0.23 to 1.07 μg L^{-1}. The method validation was performed by analyzing certified reference materials (TMDA-70 Fortified lake water, SPS-WW1 Batch 111-Wastewater, RM 8704 Buffalo river sediment, GBW07605 Tea) and spiked water samples. The method was applied to separate and determine the trace levels of Cd(II), Ni(II), Co(II), Mn(II) and Pb(II) in the well water, river water, street sediment, and tea samples.

1. Introduction

Trace metals are widely spread in the environment and may enter the food chain from the environment. Some trace metals are essential elements and play an important role in human metabolism. On the other hand, at high concentrations all metals are recognized as potentially toxic [1]. Cadmium is highly toxic even at low concentrations, causing damage to organs such as the kidneys, liver, and lungs. Nickel is a moderately toxic element and it is known that inhalation of this metal and its compounds can lead to serious problems, including respiratory system cancer [2]. Cobalt is an essential element for humans since it is present in vitamin B_{12}. This metal has also been used as a treatment for anemia because it stimulates red blood cell production [3]. Manganese plays an important role in: bone and tissue formation, reproductive functions, and the activation of many enzymes, which are involved in vital metabolic processes [4]. Lead is a harmful element. It is readily absorbed through the gastrointestinal tract. In blood, 95% of the lead is in red blood cells and 5% in the plasma. Around 70–90% of the lead assimilated goes into the bones, then liver and kidneys. It leads to renal tumors. It also interferes in the metabolism of calcium and vitamin D, affects hemoglobin formation and causes anemia. It is neurotoxin and causes behavioral abnormalities while retarding intelligence and mental development [5,6].

The determination of trace heavy metals in different environmental samples is of great interest to analytical chemists. To fulfill this need, either very sensitive instrumental techniques and/or enrichment/separation methods should be used. Flame atomic absorption spectrometry (FAAS) is one of the most widely used instruments for determination of heavy metals at trace levels due to its simplicity, operational facility, and lower cost than other instruments. However, there are some limitations in direct determination of heavy metals because of matrix interferences and insufficient sensitivity of the instrument [7–10]. Therefore, an initial preconcentration procedure is often required prior to determination of trace metal ions by FAAS.

SPE method is one of the most effective multi-element preconcentration methods because of its advantages such as ease of use, ease regeneration of solid-phase, high preconcentration factor, flexibility, low consumption of reagents, the possibility of automation, less sample handling and usually high selectivities. The choice of sorbent is a key point in SPE, because it can control the analytical parameters such as selectivity, affinity, and capacity. Therefore, preparation of new materials for selective solid-phase extraction of analytes is an important trend of solid phase extraction [11–14]. Chelating resins are superior in selectivity to solvent extraction and ion exchange due to their triple function of ion exchange, chelate formation, and physical adsorption. The functional

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group atoms capable of forming chelate rings usually include oxygen, nitrogen, and sulfur. These groups can be introduced into the polymer by chemical transformation of the matrix or by the synthesis of sorbent from monomeric ligands. The insertion of suitable specific functional groups into the polymeric matrix makes them capable of reacting with metal ions [15–17].

Polymer–metal complexes are composed of polymeric ligand and metal ions. In solution, polymer–metal complexes form microheterogeneous regions occupied by the polymer backbone, where physicochemical properties differ from those of the bulk solution. Most significant reaction patterns of polymer metal complexes are attributed to the characteristic nature of these microheterogeneous regions. Polymer metal complexes show unique characteristics in absorption spectra, coordination structures, stability, redox reactions, catalytic activities, electrochemical reactions, and other areas compared to those of corresponding low molecular metal complexes. Complexation of polymeric ligand with metal ions and ligand substitution reaction of polymer–metal complexes are used to separate metal ions and/or small molecules [18]. Polymer complexes can be obtained by mixing polymer solutions (e.g. a polyacid with a polybase) or by template polymerization. Complexation of metal ions in solution is an important process in several areas, for example, in the body design of functional groups for chelating ion-exchange materials [19], and catalysts [20]. The scope of applications of metal complexation polymers should increase considerably in the future.

Numerous studies concerning the synthesis and characterization of the selective chelating sorbents and the wide applicability of these resins in the removal of metals from various samples as well as in selective metal ion recovery processes have been published [21–23]. Gong et al. synthesized a new polyacrylacylaminourea chelating fiber and studied the properties of the chelating fiber for the preconcentration and separation of trace In(III), Bi(III), Cr(III), V(V), and Ti(IV) [24]. Colella et al. proposed a poly(acrylamidoxime) chelating resin for the concentration of trace metals from aqueous solutions [25]. Şenkal et al. described the synthesis and characterization of a thioureasulfonamide pendant resin derived from crosslinked polystyrene and used for preconcentration of Cd and Pb in water samples [26]. Tokalıoğlu et al. synthesized a new chelating resin and the resin was used for selective separation, preconcentration and determination of some trace metal ions in water samples [14]. Hazer and Kartal proposed a solid phase extraction method for the determination of Uranium(VI) in water samples. A new chelating resin including three different functional groups was used as a solid phase [27]. Segatelli et al. reported a preconcentration method using cadmium imprinted polymer prepared by bulk method [28].

In this study, poly [2-thiozyl methacrylamide (TMAAm)-co-divinylbenzene (DVB)-co-2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS)] (TMAAm-co-DVB-co-AMPS) resin was synthesized and used for the separation and preconcentration of some trace metal ions in water, street sediment and tea samples. The AMPS is a relatively strong acid [29]. The most studied interpolymer complexes are those between polybases (e.g. poly(N-vinyl-2-pyrrolidone) and polyacids-polyacrylic (PAA), poly-methacrylic (PMA) [30–32] and with poly (itaconic acid) monoesters [33]. The TMAAm as a component in copolymers with AMPS has not been previously reported. Various factors influencing the separation and preconcentration of Cd(II), Ni(II), Co(II), Mn(II) and Pb(II), such as pH, concentration of eluting reagent, flow rate, sample volume, adsorption capacity, matrix components, have been investigated.

2. Experimental

2.1. Instrument

A PerkinElmer A Analyst 800 model flame atomic absorption spectrometry (Waltham, MA, USA) equipped with hollow cathode lamps was used for the determination of Cd(II), Ni(II), Co(II), Mn(II), and Pb(II). The equipment was operated at conditions recommended by the manufacturer. Acetylene/air flow rate was 2.0/17 L min^{-1} for all the elements. The pH measurements were carried out in a WTW pH315i apparatus equipped with a combined pH electrode. The FTIR spectra of the resin were recorded on a Jasco 460 Plus FTIR spectrometer (Jasco Co., Tokyo, Japan) using a KBr disc. Elemental analyses were carried out by a Leco CHNSO-932 auto microanalyser (St. Joseph, MI, USA). The microstructure of the polymer was examined by a Leo 440 model scanning electron microscopy (SEM). Thermal data was obtained by using a Perkin Elmer Diamond TG-DTA thermobalance in N_2 atmosphere. The thermal stability of the resin was investigated by thermogravimetric analysis (TG) in a nitrogen stream at a heating rate of 10 °C min^{-1}.

2.2. Reagents and solutions

All reagents and solvents used were of analytical reagent grade. All metal stock solutions (1000 μg mL^{-1}) were prepared by dissolving an appropriate amount of their nitrate salts in 1 mol L^{-1} HNO$_3$. The working solutions were prepared by dilution of the stock solutions immediately prior to their use. The required pH adjustments were made by the use of buffer solutions. Buffer solutions were prepared by using 1 mol L^{-1} acetic acid-sodium hydroxide (pH 3–6) and 1 mol L^{-1} ammonia-hydrochloric acid (pH 8). 2-Aminothiazole (Merck, Darmstadt, Germany) and methacryloyl chloride (Alfa Easer, MA, USA) were used as received. 2,2′-Azobisisobutyronitrile (AIBN) (Merck) was purified by successive crystallizations from chloroform–methanol mixture. The crosslinker divinylbenzene (DVB) (Merck) was used as received. 2-Acrylamido-2-methyl-1-propanesulfonic acid (AMPS) (Merck) was used without further purification.
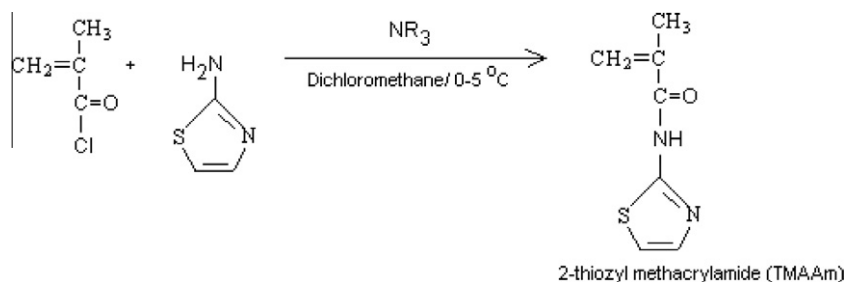

Fig. 1. Synthesis scheme of 2-thiozyl methacrylamide monomer.