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Modification of chloromethylated polystyrene with 2-mercabtobenzothiazole for application as a new sorbent for preconcentration and determination of Ag^+ from different matrices

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ABSTRACT

Chloromethylated polystyrene polymer (CMSP) modified with 2-mercabtobenzothiazole (MBT) has been developed for the selective separation and/or preconcentration of silver. The modified polymer (CMS-MBT) was characterized by elemental analysis and IR spectra. Batch and column modes were applied. The newly designed polymer quantitatively sorbed Ag^+ at pH 2 when the flow rate is 5 ml min^{-1}. The maximum sorption capacity was 0.493 mmol g^{-1} while the preconcentration factor was 250 for Ag^+. The detection limit was 8 ng ml^{-1}. The desorption was effective with 5 ml of 2 mol l^{-1} HNO_3 prior to detection using AAS. The modified polymer was highly ion-selective in nature even in the presence of large concentrations of electrolytes or organic media, with a preconcentrating ability for Ag^+. The utility of the modified polymer to synthetic and drugs samples showed RSD values of <3% reflecting its accuracy and reproducibility.

1. Introduction

Although atomic absorption spectrometry (AAS) [1,2] and inductively coupled plasma-atomic emission spectrometry (ICP-AES) [3–6] are among the most widely used methods for trace metal determination, they may be insufficient due to the matrix interferences and the very low concentration of metal ions. Therefore, a separation/preconcentration step is required. The traditional separation and preconcentration methods for metal ions include liquid–liquid extraction, co-precipitation, ion exchange, etc. These methods often require a large amount of organic solvents; some of which are harmful to health and cause problems. Recently, several methods have been used for pretreatment of the samples. Solid phase extraction (SPE) [7–12] is one of them. Its advantage is visible [13] which includes: (i) the fast, simple and direct application in very small sample amounts without loss; (ii) low risk of contamination; (iii) time and cost saving. So, SPE has been widely used for the isolation and concentration of target analytes, and the clean-up of samples (removal of matrix interferences) in pharmaceutical, clinical, environmental and food chemistry [14]. A number of solid phase extractors have been developed and tested for the removal and recovery of Ag(I) (e.g., activated carbon [15], cellulose nitrate membrane [16] and chelating resins [17]). Large improvements have been achieved in the last few years through the development of several chelating resins. The selectivity for a specific metal ion depends on what kind of complexing agent is introduced into the polymeric chain. According to the theory of hard and soft acids and bases (HSAB) defined by Pearson, metal ions will have a preference for complexing with ligands that have more or less electronegative donor atoms. Chelating agents with nitrogen and sulfur groups are highly efficient for the selective sorption of precious metal ions. Chelating resins with amine, mercaptan and thiourea groups are widely used in extraction, separation and recovery of precious metals in hydrometallurgical field.

The choice of sorbent is therefore a key point in SPE, because it can control the selectivity, affinity and capacity [18,19]. Chelating and modified polymers have found widespread applications in the separation and preconcentration of metal ions from various sources and have some advantages over SPE as higher preconcentration factor, higher selectivity, higher stability, better efficiency, and great simplicity in handling and transfer [20,21].

The increasing use of silver compounds and silver containing products in industry and medicine has resulted in an increase of environmental silver content [22,23]. Silver occurs as an impurity in copper, zinc, arsenic and antimony ores and occurs in environment through industrial waters [24]. Low-level exposure to silver compounds is widespread due to the use of soluble silver compounds to disinfect drinking water. On the other hand, recent information about the interaction of silver with essential nutrients, especially selenium, copper, Vitamins E and B12, has focused attention on its potential toxicity [25,26].

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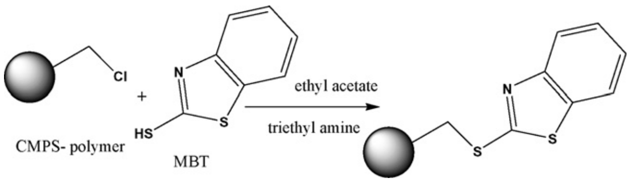

Scheme 1. Synthesis of CMPS-MBT polymer.

Due to the very low concentration of most elements, including silver, in environmental samples, their separation and sensitive determination necessitate the use of a preconcentration or trace enrichment method [27,28].

In this work, a new modified polymer is prepared by reacting mercabtobenzothiazole (MBT) with chloromethylated polystyrene polymer and its sorption behavior towards Ag^+ has been investigated in batch and column modes.

2. Experimental

2.1. Reagents

Commercial chloromethyl polystyrene copolymer (CMPS, MP-500A; Bayer Co., Germany) with divinyl benzene (2% DVB; specific surface area (BET) $66\,m^2\,g^1$ and $46\,meq\,Cl\,g^1$ resin was used. 2-Mercabtobenzothiazole (MBT) and the nitrate salts of the metal ions (Aldrich) were used. The reaction was followed up in all experiments with the aid of FTIR spectral analysis.

2.2. Apparatus

A Perkin–Elmer 2380 Atomic Absorption Spectrometer (USA) was used. The IR spectra were carried out on a Mattson 5000 FTIR Spectrophotometer (4000–400 cm^{-1}) as KBr. The UV–visible absorption measurements were performed on a Unicam 2001 UV–VIS Spectrophotometer using a 1 cm quartz cell. The pH values were measured using a pH-meter (Hanna Instruments, 8519, Italy) with an expanded scale and accuracy of ±0.01. It was standardized with 0.05 $mol\,l^{-1}$ potassium hydrogen phthalate (pH 4.01) and a standard tablet (pH 9.2) at 25 °C.

2.3. Synthesis of CSP-MBT polymer

In a 100 ml round bottom flask, 1 g of chloromethylated polystyrene soaked in dry ethyl acetate (15 ml) was added to 0.5 g of 2-mercaptobenzothiazole. The slurry was stirred vigorously for 12 h at 60 °C under reflux and the reaction mixture was filtered and washed with ethyl acetate. The librating HCl was adsorbed by nitrogen site in 2-mercaptobenzothiazole to produce ammonium salt. To remove HCl from 2-mercaptobenzothiazole bonded CMPS-polymer, 1.5 ml of triethylamine diluted in distilled water (3 ml) was added to the residue. The slurry was stirred vigorously for 2 h. The residue was then washed several times with distilled water and filtered. The resulting residue was washed with acetonitrile (50 ml), filtered and dried at 40 °C overnight and characterized by FTIR spectra and pH-metric measurements. The suggested structure of the prepared CMPSP-MBT polymer is shown in Scheme 1.

2.4. Separation procedures

2.4.1. Batch method

100 ml sample solution containing 25 $\mu g\,ml^{-1}$ of Ag^+ was transferred to a glass stoppered bottle (250 ml) and 50 mg of the modified polymer were added after adjusting its pH to the optimum value. The mixture was then shacked for 30 min with mechanical stirrer. After filtration, the modified polymer was washed with double distilled water, and the sorbed metal ion was eluted with 5 ml of a suitable concentration of HNO_3 and the resulting solution was adjusted to 100 ml and determined using AAS.

2.4.2. Column method

The modified polymer (0.5 g) was first swollen for 24 h, packed in a glass column (40 mm × 6 mm), treated with 20 ml of 1 $mol\,l^{-1}$ HNO_3 at the optimum flow rate and washed with double distilled water until the modified polymer became free from acid. A 100 ml of 50 $\mu g\,ml^{-1}$ metal ion solution buffered at the optimum pH, was passed through the column at the optimum flow rate. After sorption step, the column was washed with 100 ml of double distilled water to remove any uncomplexed metal ions from the modified polymer bed. The stripping of metals from the modified polymer was carried out by suitable eluting agent (HNO_3). The eluted solution was collected in a 100 ml calibrated flask and analyzed.

3. Results and discussion

3.1. Characterization

The active groups of MBT in the modified polymer were investigated by recording the spectra of CMPS and CMPS-MBT. The IR spectrum of CMPS exhibits a characteristic band at 701 cm^{-1} which may be attributed to C–Cl band. The presence of a broad band at 3400 cm^{-1} is attributed to ν(OH) of water. Upon modification of CMPS with MBT (Scheme 1), the band at 2600 cm^{-1} in the IR spectrum of MBT, due to ν(SH) disappear. This proves that MBT is bonded to CMPS through sulfahydryl group. The broad band centered at 1640 cm^{-1} due to ν(C=N) in MBT-CMPS is similar to that for MBT indicating that this group is not taking part in the bond formation.

The C, H and N content of MBT-CMPS was determined and the values (C = 68.20%; H = 5.23%; N = 4.80%) were compared with the calculated (C = 67.84%; H = 4.59%; N = 4.94%) to prove the modification of MBT-CMPS (97.16%). Water regain values were measured by recording the difference in weight of the modified polymer after its storage at 100 °C for 48 h. The value found to be 0.25 $g\,g^{-1}$ for MBT-CMPS. Comparison of the value with that of CMSP (0.12 $g\,g^{-1}$) indicates an appreciable improvement of the sorption capacity of the modified polymer [29].

3.2. Preliminary investigations

Batch and column preliminary experiments were carried out to investigate the quantitative sorption of Ag^+ by CMPS and MBT-CMSP. It was found that, CMSP does not show any tendency for sorption of Ag^+ ions. Alternatively, MBT-CMSP was found efficient. This is mostly due to the strong interaction between Ag^+ and the loaded organic ligand through complex formation. The analytical variables (pH, sorption kinetics, temperature and matrix effect) have been studied in detail for batch and column techniques.

3.3. Batch technique

3.3.1. Effect of pH

The effect of pH on the sorption of Ag^+ has been investigated in the pH range 1–8 (HNO_3 and NaOH were used to change the acidity of the medium).

The experiments were elaborated by shaking the solution containing Ag^+ of variable pH with the modified polymer for sufficient equilibrium time. The pH was adjusted using suitable buffer solutions. From the data represented in Fig. 1, it could be concluded that, the maximum sorption efficiency of MBT–CMPS for Ag^+ was