Synthesis a new adsorbent of molecularly imprinted polymer for absorb the silver ions from biological sample

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Abstract. This work reports the preparation of molecularly imprinted polymer (MIP) particles for selective extraction and determination of silver ions from aqueous media. Various parameters were optimized, such as pH, time, concentration of sample and type of eluent for elution of silver from polymer. Also Interfering effect was investigated on the absorption of silver by molecularly imprinted polymer. At the end, MIP verified specific selectivity of template molecule with the high detection limit. Finally, silver was preconcentrated by the synthesized molecularly imprinted in the saliva after applying of antiseptic solution. Results were compared with the obtained results by ICP method. The results showed high performance of this method in pre-concentration of silver.

Key words: molecularly imprinted polymer, solid-phase extraction, biological samples.

Introduction

Silver is an important metal in view of its high resistance to corrosion and antibacterial properties. The various compounds of this commercial metal are largely used in the medicinal and photographic industries. Despite of its wellknown usefulness properties, the toxicity of silver is characterized by a severe pulmonary edema, hemorrhage,and necrosis of bone marrow, liver, and kidney(Hosseini, and Hashemi-Moghaddam, 2005).

The widespread industrial applications of silver may result in its increased concentrations in aquatic ecosystems. Because of their bacteriostatic properties, silver compounds are often used in filters and other equipments to purify different types of water and in the processing of foods, drugs, and beverages. In many countries, silver-impregnated filters are used for drinking water preparation (Katarina et al. 2006).

Silver is considered toxic for humans and the recommendations of the World Health Organization (WHO) permit maximal concentrations of 0.1 mg L–1 of silver ions in drinking water disinfection, but the United States Environmental Protection Agency (USEPA) recommends 0.05 mg L^{-1} as maximum (Pelkonen et al. 2003). It was found that the FAAS method benefits from a high accuracy for rapid determination of trace metal analysis, but due to some limitations, it is not suitable for the direct determination of extremely low concentrations of silver in natural waters exclusive of initial separation preconcentration processing (Hosseini et al, 2007). Therefore, preconcentration and selective separation of trace or ultra-trace silver from the natural water is very important and need much more attention.

The solid-phase extraction (SPE) is being utilized for preconcentration of heavy metals due to its flexibility, economical and environmental-friendly, absence of emulsion, speed and simplicity, sampling in the field, safety and ease of automation (Thurman and Mills, 1998). The main problem associated with SPE is the low selectivity for silver. A desired grade of selectivity may be obtained using materials based on metal ion imprinted polymer (MIIP) as tailored sorbents. The selectivity of MIIP arises from the memory effect of the polymer to the imprinted ions, e.g. from the specificity of interaction of ligand with the metal ions; the coordination geometry and the coordination number of metal ions; the charge of the metal ions and to a large extent on the size of them (Wulff, 1995).

As a consequence, the ion or MIP is able to selectively recognize the template ion or molecule from other components in a sample. The synthesis of MIPs is fast and quite cheap and the material provides a high degree of molecular recognition.

At present, the imprinting of organic molecules is a well-established technology; however, few attempts have been made for ions such as trace elements. In such cases, the synthesized sorbent is called an ionic-imprinted polymer (IIP). IIPs have been mostly synthesized for recognizing lanthanides, actinides and noble metals (Roman, et al., 2008). Recently, a variety of IIPs have been prepared as selective sorbents for the SPE of heavy metals and transition elements such as copper, cadmium, cobalt, selenium and nickel (Roman, et al., 2008)

In the present work, silver dithizone-molecularly imprinted polymer was synthesized and silver adsorption conditions were investigated. Finally sliver was perconcentrated in a real sample. Results show good repeatability of synthesized polymer for silver ion adsorption.

Materials and Methods

Preparation of a molecularly imprinted polymer and the corresponding non-imprinted polymer

An MIP and a non-imprinted polymer (NIP) should be prepared in parallel and with identical compositions (except that template is to be omitted from the NIP). The procedure for the polymer synthesis was as follows:

To a three-necked round-bottom flask were added template (Ag-Dz complex in chloroform), functional monomer (MAA; 2 mmol, or 0.17 mL), cross-linker (EGDMA; 10mmol, or 1.89 mL) and initiator (AIBN; 0.25mmol, or 0.042g) in chloroform (20mL). The mixture was sparged with nitrogen for 10min to remove dissolved oxygen, which can inhibit free radical polymerization. The polymerization was allowed to continue in a water bath at 60°C for 18h. After polymerization, a hard polymer monolith was obtained, which was crushed and ground into a fine powder with a mortar and pestle. To remove templates, the remaining particles were treated with 2M of HNO_3 for 72 h, and the excess amount of HNO_3were washed by methanol. Finally the particles were dried under vacuum in a desiccator and used for the extraction studies. The dried polymer is ready for use.

Batch procedure

In 100 ml polyethylene bottles, previously cleaned with detergent, DDI water, dilute nitric acid and DDI water in sequence, added buffer solution and the metal ion solution, and immersed imprinted polymer with shaking at 25 ◦C. At pre-fixed time, an aliquot of the supernatant was separated and the silver ions were determined by FAAS. The adsorbed resin was eluted with 0.2 mol l^{-1} HCl and the desorbed Ag(I) was measured with FAAS.

Results and Discussion

The aim of this work was to evaluate the feasibility of using an imprinted polymer for the direct solid-phase extraction of silver in real samples. Two polymers were prepared and tested by batch rebinding study. The imprinted polymer (MIP) was prepared in the presence of silver, and a control polymer (NIP) was prepared under identical conditions in the absence of guest molecule.

FT-IR spectra

Control polymer and molecularly imprinted particles obtained using non-covalent imprinting protocol were subjected to characterization by FT-IR.

The FT-IR spectra of control non-imprinted and molecularly imprinted polymer materials prepared using radical bulk polymerization are shown in Figure 3. Both polymers have similar IR spectra indicating the similarity in the backbone structure.

In the IR spectra, the absorptions due to carboxyl OH stretch (ca. 3500 cm^{-1}), carbonyl group stretch (ca. 1730 cm^{-1}), C—O stretch (ca. 1260 cm^{-1}) and C—H vibrations (ca. 756,ca. 1390, ca. 1460, and ca. 2956 cm^{-1}) were observed. In addition to backbone similarity concluding, the important results were also acquired from spectra that are:

This feature is clear that absorbances attributed to the C—H stretch of methylene group (ca. 2989.15 cm^{-1}), carbonyl group stretch (ca. 1731 cm^{-1}), C—O stretch (ca. 1254 cm^{-1}) and C—H bend of CH2 (ca. 1460 cm^{-1}) for the molecularly imprinted polymer are relatively stronger than for non-imprinted polymer. From this comparison it was found that presence of imprint molecule (AgHDz complex) causes incorporation of ethylene glycol dimethacrylate in the preparation of polymer to be increased.

Choice of eluent

In order to choose the most efficient eluent, a complexing agent and various concentrations of different acids were tested. From the data given in Table 1, it is obvious that of a sulfuric acid (2M) can accomplish the quantitative elution of complex from the imprinted polymer. The volume of all eluents was 20 mL.

Table 1. Effect of type and amount of eluent on extraction efficiency

Eluent	%Recovery
H_2SO_4 (2M)	91.09
H_2SO_4 (4M)	23.98
CH_3COOH (2M)	40.74
CH_3COOH (4M)	6.29
diethyldithiocarbamate (0.01M)	40.55

Kinetics of Ag(I) sorption

Six portions of standard or sample solutions (100 mL) containing silver nitrate (0.169 mg) were transferred into 250 mL beakers. Then exactly 1 g of MIP adsorbent were added to each beaker, and the mixtures were shaken vigorously for 30, 60, 90, 120, 150 and 180 min to facilitate adsorption of the silver onto the imprinted polymer particles. After the solutions were centrifuged, the amount of non adsorbed silver in the filtrate solutions was directly determined by atomic absorption spectrophotometry. Fig. 1 shows that an equilibration time of about 150 min was required for 95% sorption. However, the time ($t1/2$) of 50% sorption was less than 20 min. It revealed that the sorption rate was slower than ordinary resins; this is derived from the high degrees of cross-linking.
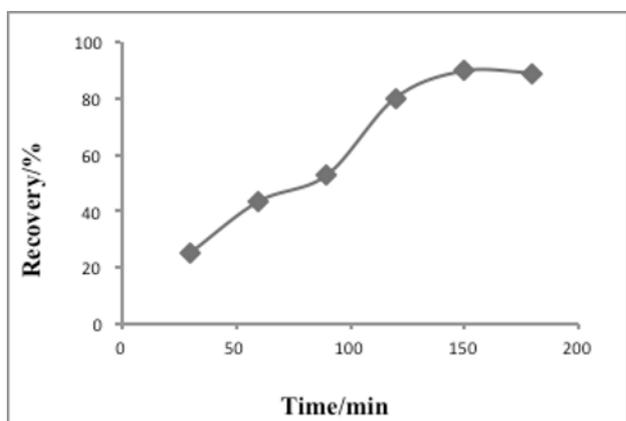

Fig. 1. Influence of adsorbing time on the adsorption capacity (initial concentration of silver equals to 1.078 mg. L^{-1}).

Effect of pH

The effect of varying pH values on Ag(I) uptake was investigated using the batch procedure. Six portions of standard or sample solutions (100 mL) containing silver nitrate (0.169 mg) were transferred into 250 mL beakers, and the pH value was adjusted in range 3-8, with 0.001 mol L^{-1}, HNO_3 or NaOH. Then exactly 1 g of MIP adsorbent was added to each beaker, and the mixtures were shaken vigorously for 150 min to facilitate adsorption of the silver onto the imprinted polymer particles. The sorption quantity of silver increases with the pH value increases. So pH 7.0 was chosen for this experiment. After pH 7.0, the sorption capacity of the polymer decreases.

Interference effects

The effect of different cations on the determination of 1.078 mg. L^{-1} silver ions by the proposed method was studied. An ion was considered interfering when it caused a variation greater than ±5% in the absorption of the
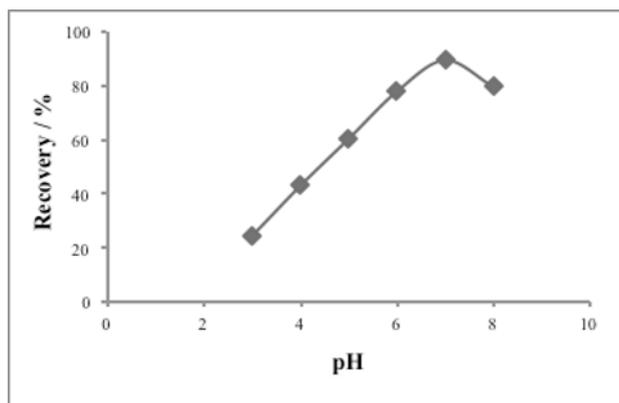

Fig. 2. Effect of pH of sample solution on Ag(I) uptake

sample. The results (Table) indicate that Ag(I) recoveries were almost high in the presence of interfering cations.

The results (Table) indicate that Ag(I) recoveries were almost high in the presence of interfering cations. Competitive adsorption of Zn(II)/Ag(I), Cu(II)/Ag(I), Ni(II)/ Ag(I), Co(II)/ Ag(I), Fe(II)/ Ag(I), Pb(II)/ Ag(I), Cd(II)/ Ag(I), Al(III)/ Ag(I) and Hg(II)/ Ag(I) from their binary mixture was also investigated in batch procedure. Although these ions posses a similar chemical property, the competitive adsorption capacity of Ag(I)-imprinted resin for Cd(II) is higher than non-imprinted resin.

The *D* values of poly-Cd(II)-DAAB-VP show increase in *D* for Cd(II), while *D* decreases significantly for Zn(II), Cu(II) and Hg(II) (Table 3). The αr values are 51.2, 45.6, and 85.4, respectively, which are greater than 1 for poly-Cd(II)-DAAB-VP of Cd(II)/Cu(II), Cd(II)/Zn(II) and Cd(II)/Hg(II). This means that Cd(II) can be determined

Table 3. The selectivity parameters of imprinted polymer for Ag(I)

Metal ions	D_i	D_n	α_i	α_n	α_r
Ag^+	1850	18			
Ni^{2+}	59.63	8	31.02	2.25	13.78
Cu^{2+}	39.64	14	46.67	1.28	36.46
Co^{2+}	29.46	12	62.78	1.5	41.85
Fe^{2+}	20.01	13	69.73	1.38	50.52
Zn^{2+}	22.02	14	83.99	1.28	65.61
Pb^{2+}	24.48	12	75.56	1.5	50.37
Cd^{2+}	28.99	9	63.80	2	31.9
Al^{3+}	21.73	14	85.10	1.28	66.48
Hg^{2+}	34.25	15	54	1.2	45

Determination of Ag(I) ions in real sample

The real sample was saliva sample after applying of antiseptic solution. 5 mL from this sample was added to 10 mL of concentrated nitric acid. Then, the pH value was adjusted on 7.0. Afterwards, 10 min was heated at 70° C and the volume of solution was to 50 mL. Then exactly 1 g of MIP adsorbent was added to solution, and the mixtures were shaken vigorously for 150 min to

facilitate adsorption of the silver onto the imprinted polymer particles.

The amount of silver was measured in the saliva after pre-concentration by the synthesized molecularly imprinted polymer and results were compared with the ICP method. The results show high performance of this method in pre-concentration of silver.

Table 3. Analysis of real Sample

Method	Concentration (mg/L)
ICP	0.017
MIP-ASS	0.114

Conclusion

In this study, the use of a MIP for SPE as an alternative method to other techniques of the separation and pre-concentration of Ag offered several advantages including low cost, high capacity with high recovery, very good extraction efficiency and this method provides selective, simple and practical strategy for the determination of silver. The strategy involves preparation of silver-selective polymer via a non-covalent molecular imprinting approach and then using the final particles for solid phase extraction. The proposed pre-concentration method was suitable for repeated use without considerable loss of adsorption capacity and revealed a good detection limit.

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