Selective magnetic mercury (II) ion capturing ligand-doped silica gel for water analysis

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Preparation of selective magnetic adsorbents for the dispersive micro-solid phase extraction often involved multistep reactions which are time-consuming. This study demonstrated a simplified method for the synthesis of a magnetic adsorbent, which is selective towards the adsorption of mercury (II) ion (Hg²⁺). In this method, the incorporation of metal capturing ligand (3-oxo-1,3-diphenylpropyl-2-(naphthalen-2-ylamino) ethylcarbamothioate) and the coating of magnetic particles with silica gel was performed in a single step. This adsorbent was then used in solid-phase microextraction for the preconcentration of Hg²⁺ in water. In this study, mercury analyzer was used to quantify the Hg²⁺. Under optimized condition, the developed analytical method achieved low method detection limit (4.0 ng L⁻¹), satisfactory enrichment factor (96.4), wide linearity range (50.0 - 5000 ng L⁻¹) with a good coefficient of determination (0.9985) and good repeatability (<7%). The preconcentration factor of this method was 100. This proposed method was also successfully utilized for the determination of Hg²⁺ in drinking water, tap water and surface water with good recovery (>91%) and high intra-day and inter-day precision.

Introduction

Mercury is among the most hazardous metals to living organisms. World Health Organization reported that mercury that detected in drinking water is present in the form of Hg²⁺ and Hg⁰. Inorganic mercury (Hg⁰ and Hg²⁺) is also found to accumulate in the kidney and cause kidney damage. The United States Environmental Protection Agency has established a maximum contaminant level goal (MCLG) of 2 µg L⁻¹ for inorganic mercury in water to protect human health. The concentration of total dissolved mercury in natural water samples could vary from pg L⁻¹ to ng L⁻¹. Therefore, to determine the Hg²⁺ contamination in natural water, an appropriate preconcentration procedure is often required. Although Hg²⁺ at low levels may not cause the harmful effect to the living organism, however, the determination Hg²⁺ at this level could allow the detection of Hg²⁺ contamination in natural water before it reaches the dangerous level.

Dispersive micro-solid phase extraction (D-µSPE) is an alternative method for solid phase extraction which allows the dispersion of adsorbent in liquid matrices with the aid of agitation. As compared to conventional SPE, the close contact between the adsorbent particle and analyte enhances the kinetics of sorption and consequently improve the efficiency of extraction. The application of solid phase extraction method that employing modified magnetic particles as the adsorbent in analytical chemistry has increased significantly in recent years. Conventional dispersive micro-solid phase extraction (D-µSPE) required the laborious and time-consuming procedure for retrieving the adsorbent from water matrices after extraction. However, when magnetic particle-based adsorbents are used, their superparamagnetic properties allow it to be separated from water by an external magnetic field. As a result, the duration of sample preparation can be significantly shortened. Recently, a wide range of magnetic adsorbents has been developed for the selective determination of Hg²⁺. Most of these magnetic adsorbents were produced through a series of reactions that include the synthesis of magnetic nanoparticles (MNP), the coating of MNP with the silica gel, functionalization of silica gel and followed by the bonding of selected ligand. Some of these reactions also involved higher temperature reflux and are time-consuming.

Among the various type of adsorbent, metal capturing ligand-incorporated sol-gel has been reported as one of the effective adsorbents for metal ions removal. This material has become an attractive adsorbent due to its simplicity in preparation. The incorporated metal capturing ligands in silica gel matrix can retain its efficiency to complex with metal ions. This study demonstrated the coating of silica gel doped with metal capturing ligand onto MNP to produce a solid adsorbent for D-µSPE. This method simplifies the preparation of magnetic adsorbent by incorporating the metal capturing ligand during the coating of MNP with the silica gel. In this study, 3-oxo-1,3-diphenylpropyl-2-(naphthalen-2-ylamino)-ethylcarbamothioate (ODE) was selected as Hg²⁺ capturing ligand. A previous study has proven the high selectivity of ODE incorporated sol-gel in the removal of Hg²⁺ from the water. The main objectives of this study were to prepare MNP that coated with ODE incorporated sol-gel and to develop a preconcentration method for Hg²⁺ in drinking water and surface water by using ODE incorporated MNP based magnetic dispersive solid phase extraction (MDSPE).