Available online at www.sciencedirect.com
ScienceDirect
Journal of Environmental Sciences 2013, 25(6) 1252–1261
JOURNAL OF ENVIRONMENTAL SCIENCES
ISSN 1001-0742
CN 11-2629/X
www.jesc.ac.cn

Chemically modified silica gel with 1-{4-[(2-hydroxy-benzylidene)amino]phenyl}ethanone: Synthesis, characterization and application as an efficient and reusable solid phase extractant for selective removal of Zn(II) from mycorrhizal treated fly-ash samples

R. K. Sharma[1,*], Aditi Puri[1], Anil Kumar[1], Alok Adholeya[2]

1. Green Chemistry Network Centre, Department of Chemistry, University of Delhi, Delhi-110007, India
2. Biotechnology and Management of Bioresources Division, The Energy and Resource Institute, New Delhi-110003, India

Received 11 September 2012; revised 24 December 2012; accepted 21 January 2013

Abstract

1-{4-[(2-hydroxy-benzylidene)amino]phenyl}ethanone functionalized silica gel was synthesized and used as a highly efficient, selective and reusable solid phase extractant for separation and preconcentration of trace amount of Zn(II) from environmental matrices. The adsorbent was characterized by fourier transform infrared spectroscopy (FT-IR), elemental analysis, ^{13}C CPMAS NMR spectroscopy, scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and BET surface area analysis. The dependence of zinc extraction on various analytical parameters such as pH, type and amount of eluent, sample flow rate and interfering ions were investigated in detail. The material exhibited superior adsorption efficiency for Zn(II) with high metal loading capacity of 1.0 mmol/g under optimum conditions. After adsorption, the recovery (> 98%) of metal ions was accomplished using 1.0 mol/L HNO_3 as an eluent. The sorbent was also regenerated by microwave treatment in milder acidic environment (0.1 mol/L HNO_3). The lower detection limit and preconcentration factor of the present method were found out to be 0.04 μg/L and 312.5 respectively. The modified silica surface possessed excellent selectivity for the target analytes and the adsorption/desorption process remained effective for at least ten consecutive cycles. The optimized procedure was successfully implemented for the extraction of Zn(II) from mycorrhizal treated fly ash and pharmaceutical samples with reproducible results.

Key words: solid phase extraction; silica gel; preconcentration; fly-ash; zinc

DOI: 10.1016/S1001-0742(12)60173-9

Introduction

Zinc has a fundamental role in the structure and function of numerous proteins, including metalloenzymes, transcription factors and hormone receptors. The widespread role of zinc in metabolism is also accentuated by the occurrence of zinc in all tissues, organs and fluids of the human body (DeMartino et al., 2010). In addition to this, since the industrial revolution, the use of zinc has increased exponentially due to its presence in every area of modern consumerism: from construction materials to cosmetics, medicines to processed foods and appliances to personal care products (Pérez-Quintanilla et al., 2009; Yu and Li, 2011). The extensive utilization and application of zinc in various industrial and commercial activities necessitates its accurate analytical determination and recovery for regulating and minimizing its discharge into the environment from the view point of safety. This is because elevated quantities of zinc in living organisms have been reported to cause various acute and chronic adverse effects, reduction in growth reproductive and developmental defects, electrolyte imbalance, nausea lower levels of high-density lipoprotein cholesterol, intracellular production of reactive oxygen species (ROS), and in consequence, oxidative stress or death of cells (Environmental Health Criteria Document 221 Zinc, 2001; US EPA, 2005). To conquer the rising concern of zinc toxicity, various preconcentration techniques such as ion pair extraction (Malvankar and Shinde, 2007), precipitation (Lenz and Martins, 2007) and liquid-liquid extraction (Shukla and Rao, 2002) are being practiced over decades. But, these methods are

* Corresponding author. E-mail: rksharmagreenchem@hotmail.com

not economical and eco-friendly and suffer from various drawbacks like lack of sensitivity and selectivity and use of large amount of toxic organic solvents which have deleterious effect on human health and environment. Thus, solid phase extraction (SPE) has come to the forefront in recent years for selective preconcentration and separation of trace amounts of elements as it simplifies labour intensive sample preparation, lessens the cost and time, eliminates the clean-up step, provides high enrichment factors, and minimizes costs due to low consumption of reagents thus providing an economic, persuasive and greener alternative to other traditional methodologies (Sharma et al., 2003)

In continuation of our research work (Sharma et al., 2012b, 2005, 1999a; Garg et al., 1999b; Sharma and Dhingra, 2011; Sharma and Pant, 2009a, 2009b; Sharma and Goel, 2005; Sharma, 2001) on synthesis of efficient and cost effective solid adsorbents having specific metal ion binding affinity against background constituents, the present work is focused on the synthesis of schiff's base functionalized silica gel with a view of finding out a simple and extremely selective solid phase extractant for Zn(II) ions. In fact, a comparative data of the present work with some literature precedents, based on ligand-functionalized amorphous and mesoporous silica materials for zinc adsorption has been compiled in **Table 1**. It is evident from comparison that the synthesized adsorbent exhibits enhanced analytical characteristics with respect to most of the chelating resins based on different silenous matrix. Although, MTTZ-MCM-41 was able to bind quantitatively more Zn(II) ions from aqueous solution, the preconcentration factor was low. Moreover, adsorbent could not be reutilized for more than three successive adsorption-desorption cycles.

The applicability of the present method is judged by investigating the uptake behavior of the adsorbent for zinc in fly ash samples from two major fertilizer and thermal power plants of North India. Indian coal used in fertilizer or thermal power plants generates massive contents of fly ash which are generally being considered a deadly source of health hazards because of the presence of potentially toxic concentrations of heavy metals (Hansen et al., 2002). Land fill disposal of fly ash has adverse impacts on terrestrial and aquatic ecosystems due to leaching of toxic metal ions into soil and groundwater. Therefore, the extraction of metals from fly ash is of utmost concern to cease the environmental transitions caused by these metal loaded dumps. Major initiatives have been taken up by TERI (The Energy and Resources Institute) to ecore-store these ash containing lands. These hazardous sites have been reclaimed to reduce the leachable content of heavy metals through the implementation of mycorrhizal fungi-based technology (Pandey et al., 2009; Gaur and Adholeya, 2004; Sharma et al., 2012a). We have examined and compared the concentration of zinc left in the areas after mycorrhizal treatment with non treated ash dumps. Subsequently, we have implemented the outlined method for effective and selective uptake of residual zinc content from these samples. To best of our knowledge, this type of applicability has not been elucidated before for solid phase extraction of zinc.

1 Materials and methods

1.1 Reagents

4-Amino acetophenone, silica gel and salicylaldehyde were procured from Sisco Research Laboratory and used as received without further purification. 3-Aminopropyltriethoxysilane (APTES) was purchased from Sigma Aldrich. Working solutions were prepared by appropriate dilution of the stock standard solutions.

Table 1 Comparison of important analytical characteristics of various chelating matrices used for the separation and preconcentration of Zn(II) ions

Immobilized ligand	Support material	Adsorption capacity (mmol/g)	Preconcentration factor	Reference
5-Mercapto-1-methyltetrazole	MSU-2 and HMS	0.94 and 0.72	200	Pérez-Quintanilla et al., 2010
Sulfanilamide	Silica Gel	0.292	100	Zou et al., 2009
5-Mercapto-1-methyltetrazole	SBA-15	0.96	200	Pérez-Quintanilla et al., 2009
3-Aminopropyltriethoxysilane	Mesoporous silica	0.36	–	Yang et al., 2008
5-Mercapto-1-methyltetrazole	MCM-41	1.59	100	Pérez-Quintanilla et al., 2007
Polyamidoamine and EDTA-polyamidoamine	SBA-15	0.21 and 0.15	–	Jiang et al., 2007
Curcumin	Silica Gel	0.37	75	Zhu et al., 2007
2,3-Dihydroxybenzaldehyde	Silica Gel	0.133	–	Alan et al., 2007
Cyanex 272	SBA-15	0.111	–	Northcott et al., 2006
2-Aminomethylpyridine	Silica Gel	0.22	–	Sales et al., 2004
o-Dihydroxybenzene	Silica Gel	0.168	–	Venkatesh et al., 2004
PEI	Silica Gel	0.82	–	Ghoul et al., 2003
8-Hydroxyquinoline	Silica Gel	0.177	200	Goswami et al., 2003
Resacetophenone	Silica Gel	0.191	150	Goswami et al., 2002a
1,4-Bis-[3-(trimethoxysilyl)propyl]ethylenediamine	HMS	0.0011	–	Hossain et al., 2002
Cyanex 272	Silica Gel	0.31	–	Chah et al., 2002
1,8-Dihydroxyanthraquinone	Silica Gel	0.18	–	Goswami et al., 2002b
1-{4-[(2-Hydroxy-benzylidene)amino]phenyl}ethanone	Silica Gel	1.004	312.5	This work