Ultrasonics - Sonochemistry 40 (2018) 265–270

Contents lists available at ScienceDirect

Ultrasonics - Sonochemistry

journal homepage: www.elsevier.com/locate/ultson

Ultrasonic-energy enhance the ionic liquid-based dual microextraction to preconcentrate the lead in ground and stored rain water samples as compared to conventional shaking method

Sooraj Nizamani, Tasneem G. Kazi*, Hassan I. Afridi

National Centre of Excellence in Analytical Chemistry, University of Sindh, Jamshoro 76080, Pakistan

ARTICLE INFO

Keywords:
Lead
Ultrasound energy
Electrical shaker
Ionic liquid
Dual microextraction
Ground and surface water

ABSTRACT

An efficient preconcentration technique based on ultrasonic-assisted ionic liquid-based dual microextraction (UA-ILDμE) method has been developed to preconcentrate the lead (Pb^{+2}) in ground and stored rain water. In the current proposed method, Pb^{+2} was complexed with a chelating agent (dithizone), whereas an ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate) was used for extraction purpose. The ultrasonic irradiation and electrical shaking system were applied to enhance the dispersion and extraction of Pb^{+2} complex in aqueous samples. For second phase, dual microextraction (DμE phase), the enriched Pb^{+2} complex in ionic liquid, extracted back into the acidic aqueous solution and finally determined by flame atomic absorption spectrometry. Some major analytical parameters that influenced the extraction efficiency of developed method, such as pH, concentration of ligand, volume of ionic liquid and samples, time of shaking in thermostatic electrical shaker and ultrasonic bath, effect of back extracting HNO_3 volume, matrix effect, centrifugation time and rate were optimized. At the sample volume of 25 mL, the calculated preconcentration factor was 62.2. The limit of detection of proposed procedure for Pb^{+2} ions was found to be 0.54 μg L^{-1}. The validation of developed method was performed by the analysis of certified sample of water SRM 1643e and standard addition method in a real water sample. The extraction recovery of Pb^{+2} was enhanced ≥ 2% with shaking time of 80 s in ultrasonic bath as compared to used thermostatic electrical shaker, where for optimum recovery up to 10 min was required. The developed procedure was successfully used for the enrichment of Pb^{+2} in ground and stored rain water (surface water) samples of an endemic region of Pakistan. The resulted data indicated that the ground water samples were highly contaminated with Pb^{+2}, while some of the surface water samples were also have higher values of Pb^{+2} than permissible limit of WHO. The concentration of Pb^{+2} in surface and ground water samples was found in the range of 17.5–24.5 and 25.6–99.1 μg L^{-1} respectively.

1. Introduction

Human activities enhance the level of heavy metals including lead (Pb^{+2}) in the environment of industrial developed countries. The discharge of huge amount of heavy metals into the atmosphere creates adverse impacts on human and animal's health [1–3]. These metals are introduced into different water bodies i.e. rivers, lakes, groundwater and streams through the different processes, acid mine drainage, combustion of fossil fuels, and smelting of sulfide ore. The ingestion of Pb^{+2} via drinking water is generally due to the corrosion of metallic pipe lines of supply system, where it is frequently used for this purpose [4,5]. The EPA (environmental protection agency) recommended upper limit of Pb^{+2} in drinking water is 15.0 μg L^{-1}, while the guideline value given by world health organization (WHO) is 10 μg L^{-1} [6,7].

The Pb^{+2} is known to be a very harmful element for animals as well as human beings. The Pb^{+2} might be considered as highly toxic metal that accumulates in the human body all over the life [8]. At higher exposure/intake of Pb^{+2} creates adverse affects on the individuals of almost all ages but children are more effected [9]. Some distinctive indications of Pb^{+2} poisoning are abdominal pain, headaches, anemia, hematological damage, kidney malfunctioning, whereas the most important effects is on the central nervous system especially of children [10,11]. The toxic characteristics of Pb^{+2} is responsible for the immense research, about its exposure and effects on humans, and other living organisms.

The determination of trace metal ions has been performed through flame atomic absorption spectrometry (FAAS), mostly due to its simplicity and cost effectiveness [12,13]. Though, direct analysis of trace

* Corresponding author.
E-mail addresses: soorajnizamani@gmail.com (S. Nizamani), tgkazi@yahoo.com (T.G. Kazi), hassanimranafridi@yahoo.com (H.I. Afridi).

http://dx.doi.org/10.1016/j.ultsonch.2017.07.024
Received 20 May 2017; Received in revised form 14 July 2017; Accepted 15 July 2017
Available online 15 July 2017
1350-4177/

quantity of metal ions using FAAS is inadequate, might be due to low sensitivity and interference of complex samples matrix [14,15]. For the determination of trace levels of Pb^{+2}, preconcentration steps prior to the analysis are required [16]. Several preconcentration techniques for the separation and enrichment of trace levels of Pb^{+2} have been developed including cloud point extraction, liquid–liquid extraction and solid-phase extraction [17–22]. Recently an efficient microextraction technique, named as dispersive liquid–liquid microextraction based on a ternary component solvent was developed [23]. The ionic compounds consists a class known as ionic liquids (ILs), that have many unique physical and chemical characteristics such as, non-flammability, miniature vapor pressures and melting points, excellent thermal stabilities, broad liquid ranges, efficiently extracts organic compounds and metal ions as neutral or charged complexes [24–26].

Currently, ultrasound energy has gained substantial attention due to its low cost and greener nature for the researchers to be used as a safe force to disperse the solutions [27]. Ultrasound energy enhances the mass transfer and the contact area between two media by producing cavitation effect in solution, while propagating through the solution due to the physical phenomena like micro-streaming, micro-turbulence, acoustic (or shock) waves and micro-jets [28]. As consequence of the cavitation phenomena, when a slurry is subjected to ultrasonic irradiation, the analyte present in the solid may be extracted into the liquid media. Several preconcentration methods with the aid of ultrasound energy have been developed. Among them, ultrasonic assisted ionic liquid based microextraction is well-developed method. The IL based dispersive process accelerates with the aid of ultrasonic radiation, enhance the migration of analyses into fine droplets of IL and also increases the extraction yields [29–31]. Ultrasound-assisted emulsification and liquid–liquid extraction have been more beneficial might be due to quick extraction equilibrium is developed in a very short time [32].The viscous analyte containing IL phase needed to be dispersed by some sort of energy, which could be applied by different sources such as electrical and ultrasound energy assisted agitation [33].

The purpose of current study is to develop an efficient and reliable method, using ultrasound energy to enhance the extraction and dispersion of sample solutions in IL for the extraction of Pb^{2+} ions in real ground and surface water samples obtained from different areas of Thar Desert, Pakistan. The obtained results were compared with those values obtained by electrical shaking system on same standards/real samples. The important feature of developed method was to eliminate the adverse effect of IL via back extraction of analyte in aqueous acid solution, before analysis with FAAS. Various variables under the optimum experimental values were studied in detail.

2. Experimental work

2.1. Description of sampling area

Tharparkar is in the southeastern part of Pakistan covering approximate 19,638 Km^2 and it consists of different sub-districts, Chachro, Diplo, Nagarparkar and Mithi, situated in Sindh, and positioned between 24° 44′ 24″ N, 69° 48′ 0″ E. The whole area is enclosed by small and big dunes of sand with sharp bushes and it has a dry and humid desert climate with temperature range 9–48 °C, with average rainfall of 350 mm. The people of Tharpakar district generally use groundwater for drinking and domestic purpose. The groundwater tapped by dug wells is brackish to saline and available at the depth of 40–250 ft. The major issues of the population of Tharparkar are waterborne diseases and poor socioeconomic condition, most of them living in villages have low literacy rate with inadequate basic health necessities [34].

The drinking water in Tharparkar has different sources, which involve 93.9% wells, 2.26%, 1.66% and 0.69% of tube wells, hand pumps, stored rain water ponds, respectively and 1.47% of other sources. The study area have prosperous of minerals resources e.g. granite, china clay, salts, and coal, hence the ground water is brackish and unfit for human consumption. There is no any large industry in the immediate vicinity of sampling sites. In understudy region, rainwater is generally reserved in specially prepared big ponds for drinking and agricultural purposes.

2.2. Chemicals and glasswares

All the reagents used were of analytically grade and the solutions were made in ultrapure purified water obtained from ELGA lab water system (Bucks, UK). The conc HNO_3 (purity 65%) was purchased from Merck (Darmstadt, Germany). 0.5% of diphenylthiocarbazone (dithizone) was made in 100 mL of ethanol Sigma-Aldrich (St. Louis, MO, USA). (Dithizone) was bought from Merck. Ionic liquid [C_4MIM] [PF_6] of Sigma-Aldrich was used in the developed method. The 0.2 mol L^{-1} of HNO_3 was used to make working standards solutions by dilution of the stock standard solution (Fluka Kamica). The pH was adjusted from 2 to 9 by drop wise addition of 0.1 mol L^{-1} of hydrochloric acid/sodium hydroxide in acetate and phosphate buffer (monitored with a pH meter). The precision of the proposed method, a certified reference material of water NIST SRM − 1643e (Gaithersburg, MD, USA) was employed.

2.3. Instrumentation

Flame atomic absorption spectrophotometer of Perkin-Elmer Model A Analyst 700 (Norwalk, CT) was applied for analysis of standards and samples. Energy source (hollow cathode lamp) of Pb^{+2} which has 7.0 mA of current and 0.7 nm of spectral band width was put to work during analysis. The wavelength for analysis of Pb^{+2} was selected to be 283.3 nm. To obtain the maximum absorbance signal of analyte, oxidant and acetylene flow rates as well as burner height were adjusted properly. pH and conductivity of water samples were measured by pH meter (Ecoscan Ion 6, Malaysia) and conductive meter (InoLab conduc. 720, Germany), respectively. To centrifuge the solutions, a WIROWKA Laboratory jna type WE-1, nr-6933 (Mechanika Phecyzyjna, Poland), with speed and time ranged from 0 to 6000 rpm and 0 to 60 min, respectively, was used. An end-over-end electrical shaker (Gallankamp, Germany) was used for shaking. A programmable ultrasonic water bath, with temperature of 0–80 °C at ultrasound frequency of 35 kHz was used for incubation (model No. SC-121TH Sonicor, Deep Park, NY, USA).

2.4. Sampling

The groundwater samples have been collected during 2015–16, from twenty-four (24) villages of 4 sub-districts of Tharparkar (n = 10–20 of each). The sampling points were marked with global positioning system. The water samples were collected from dug well with the depth greater than 40 ft, manually. The surface water (stored rainwater) samples have been collected during (2015–2016) from 4 sub-districts of Tharparkar. The collected water samples were stored in precleaned polyethylene plastic bottles with 10% HNO_3 and ultrapure water.

2.5. Procedure for ultrasound assisted ionic liquid-based dual microextraction (UA-ILDμE)

The outline of developed UA-ILDμE method is represented in graphical abstract. For experimental work, two sets of replicate working standard solutions (10 μg L^{-1}) of Pb^{+2} ions (10 mL), while triplicate samples of each ground and surface water samples (25 mL) were taken in centrifuge tubes (50 mL in capacity), separately. The complexing agent, dithizone (1 mL) in the range of (0.1–0.5%) and acetate/phosphate buffer (2 mL) were added to maintain the pH from 2 to 9 with the addition of 0.1 mol L^{-1} HCl/NaOH. Then added 50–200 μL of IL