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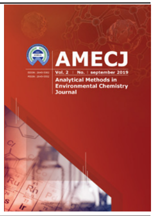

Separation and determination of lead in human urine and water samples based on thiol functionalized mesoporous silica nanoparticles packed on cartridges by micro column fast micro solid-phase extraction

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ABSTRACT

An efficient method based on thiol functionalized mesoporous silica nanoparticles (HS-MSNPs) was used for extraction of lead ions (PbII) from urine and water samples by packed column micro solid phase extraction (PC-MSPE). By procedure, 15 mg of HS-MSNPs packed in syringe cartridges (SC, 5mL) with cellulose membrane and pH adjusting at 5.5-6.5. Then, the lead of urine and water sample was efficiently extracted on HS-MSNPs after pushing the plunger of a syringe. Finally, the Pb (II) was back-extracted with inorganic acid solution and the remained solution determined by electrothermal atomic absorption spectrometry (ET-AAS). By optimization conditions, the enrichment factor, LOD, linear range and RSD% was obtained 24.8, 0.04 μg L^{-1}, 0.12-5.5 μg L^{-1} and less than 5%, respectively for 5 mL of urine samples. The validation was confirmed by spiking of real samples and using certified reference material (CRM, NIST) in water and urine sample.

1. Introduction

Heavy metals such as; arsenic (As), lead (Pb), Cobalt (Co), chromium (Cr) and mercury (Hg) and nickel (Ni) with densities about 5 gram per cubic centimeter are called heavy metals. Natural and human sources of heavy metals are mineral resources development, metal processing and smelting, petrochemical company, factory emissions, and sewage irrigation [1]. Exposure to heavy metals especially mercury caused to different disease in humans. For example, disorders of the cardiovascular, CNS, Liver, renal, and others, may be lead to dangers acute and chronic disease such as, cancer and multiple sclerosis [2-5]. So heavy metals enter to human body and cause many problem with adverse health effects [6]. Heavy metals have a normal range in environment (air, soil, water), but industrial activity increase their concentrations in the environment matrix and humans [7]. The Pb(II) was widely used in industrial processes and has highly toxic effect in humans as a major environmental pollutant [8]. In battery factory, the lead exposure is still the main subject in the human workplace and occupational health but some

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protective instruments used to reduce the emission of lead [9-11]. Lead is used for pipe, instruments and medical device as a resistant to corrosion and X-ray. The lead with melting point of 327 °C and evaporation pressure out 1.77 mmHg was used in industrial process with different application such as, battery, ceramic, balls, rubber, crystals, and pesticide [12]. The international agency for research on cancer (IARC) reported, the inorganic and organic lead caused to carcinogenic effect in humans [7, 12, 13]. Also, the half-life of Pb in blood, soft tissue and bone was obtained about 35 days, 50 days and 20 years, respectively [6, 14, 15]. The previously papers showed that, the lead poisoning has adverse health effects in human systems and acute and chronic exposure caused to disorder in cardiovascular, digestive, and nervous systems [12]. Car exhausts, contaminated food, industrial emission, and air and soil pollution could be a good example of lead exposure by skin, inhalation or ingestion. Symptoms of lead toxicity included, abdominal pain, anorexia, tremor, CNS problem, MS, constipation, myalgia, irritability, and anemia. Lead poisoning can be caused an acute abdominal pain [16, 17]. The toxicity of lead evaluates in the blood, hair, urine, and stool samples by ET-AAS or ICP instruments. Lead can be excreted in urine by the renal, so, nephrotoxicity was occurred in both acute and chronic exposure of lead in adults and children's. The nephrotoxic effects of lead has been observing at high blood concentrations 1.93 -2.42 µmol L^{-1} (40-50 µg dL^{-1}) [15, 18]. The various methods was used for determination lead in different matrix samples [13, 19]. The most well-known methods are; flame atomic absorption spectrometry (FAAS) [20], graphite furnace atomic absorption spectrometry (GFAAS) [21], inductively coupled plasma-optical emission spectrometry (ICP-OES) [13], and inductively coupled plasma-mass spectrometry (ICP-MS) [22]. Due to the low concentration of lead in biological matrix, interferences ions and difficulty analysis of lead, a sample preparation step before the determination process is necessary [23, 24]. Liquid-liquid extraction/micro extraction(LLE/LLME) [25], co-precipitation [26], cloud point extraction(CPE) [27], and solid-phase extraction/micro solid-phase extraction (SPE&MSPE) [28] are the most effective pre-concentration procedures. Also, different sorbets were evaluated for SPE methods. Recently, nanosorbents as favorite sorbent was considered for extraction heavy metals in water and human samples [29]. As reliable analytical performance for metal adsorption /determination, a variety of nanomaterials include; modified macromolecules [28], carbon nanotubes [30], magnetic materials [31], mesoporous materials [32], and ion-imprinted polymers [33], ferric oxide [34], titanium oxide [35], manganese oxide [36], and aluminum oxide [37] have been used in SPE. Nanomaterials with high surface area, high adsorption, usability, good recovery, low time extraction are candidate for SPE analytical approach[13]. Some advantages such as high sensitivity, low sample requirement, low solvent consumption, simplicity, and easy automation, Solid-phase micro extraction (SPME) as successful technique has been used for extraction metals from liquid phase [38]. Other nanomaterials include; polymer nanoparticles, nanocarbon, nanozeolites, functionalized nanomaterials and mesoporous silica nanoparticles was used as efficient sorbent for extraction heavy metals by SPE or MSPE [39]. Due to excellent dispensability and high adsorption capacity with large specific surface area, mesoporous silica based on monolithic column have attracted by SPE/SPME procedure [40]. For analyzing heavy metals based on SPE method, various functionalized mesoporous silica with thiol, amine, phosphonate, etc. have been used. Recently, the syringe-based SPE device containing thiol and amine functionalized mesoporous silica was used for the simultaneous uptake of As(III) and As(V) in liquid samples [38, 40]. In this work, lead in urine and waters were extracted based on HS-MSNPs by PC-MSPE technique before determined by ET-AAS. By proposed method, HS-MSNPs as an adsorbent were validated by CRM. The thiol functionalized MSNPs was used as complexing agent for extraction of lead from samples. The chemical bonding of HS-MSNPs was occurred based on the thiol-lead bonding by sorbent in liquid phase.

2. Material and method

2.1. Apparatus and Reagents

The ultra-pure reagents such as, sodium hydroxide (NaOH), hydrogen peroxide (H_2O_2), inorganic and organic acids(H_2SO_4, HNO_3, HCl, CH_3COOH), T-ethoxysilane (TEOS, CAS N: 800-6580025), Triethanolamine hydrochloride ($TEAH_3$, HOCH2CH2)3N , HCl, CAS N: 102-71-6), hexadecyltrimethylammonium bromide as ammonium surfactant; (CTAB, $C_{19}H_{42}BrN$, N: 57-09-0), sodium hydroxide, lead nitrate salt (CAS number: 10099-74-8) and - 3-Triethoxysilyl-1-propanethiol ($C_9H_{22}SO_3Si$, CAS N: 14814-09-6) was purchased from Sigma Aldrich (Darmstadt,Germany). Sodium silicate solution ($Na_2O(SiO_2)_x \cdot xH_2O$, N: 338443, Sigma Germany), pure ethanol solution and acetone were prepared from Merck(Germany). The standard solution of Pb(II) was prepared from the lead chloride [liquid of Pb Cl_2] as 1 g L^{-1} solution in HCl 1%. The micro gram concentrations of Pb Cl2 were prepared daily by dilution HCl. For evaluation of the purity of HS_ MSNPs, toxic metals such mercury; lead determined by ET-AAS. The pH of samples was adjusted by buffer solutions. The CH_3COONa/ CH_3COOH and ammonium buffer solutions were selected for pH of 3-7and 7.5-10. The results were obtained by electrothermal atomic absorption spectrometer (GBC, ET-AAS, Australia). A deuterium background correction lamp (UV) and hollow cathode lamp with 5 mA and a wavelength of 283.3 nm was adjusted. The pH of samples was determined by pH meter of Metrohm, Germany.

2.2. Synthesis of thiol functionalized MSNPs

In a typical synthesis, tri-ethoxysilane was added to predetermine amounts of Triethanolamine hydrochloride. The solution was heated up to 140 °C under vigorous stirring. After cooling down to 90 °C, CTAB was added to this solution. The final molar compositions of the reactants were 1.0 TEOS: 3.5 $TEAH_3$: 0.25 CTAB: 90 H_2O [41-43]. For thiol functionalization of calcined MSNPs, 1.4 g of 3-mercaptopropyltriethoxysilane ($C_9H_{22}SO_3Si$) and 1.5 g of calcined MSNPs in presence of toluene, were refluxed for 24 h and then washed with DW. The obtained thiol functionalized MSNPs (HS_ MSNPs was dried at 75°C.

2.3. Characterization

The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) was used for morphology and size morphology of the HS-MSNPs by Philips Co., Netherland (model PW3710 & model CM30) (Fig. 1a and b). The elemental analyzer was used for determination of elemental composition ratio H/C, N/C, S/C or C/N (GBC, AUS). X-ray diffraction (XRD) peak of HS-MSNPs and MSNPs were obtained with by wavelength 0.15 nm (Fig. 2) (Seifert TT 3000, Germany). Functional groups of SH on MSNPs

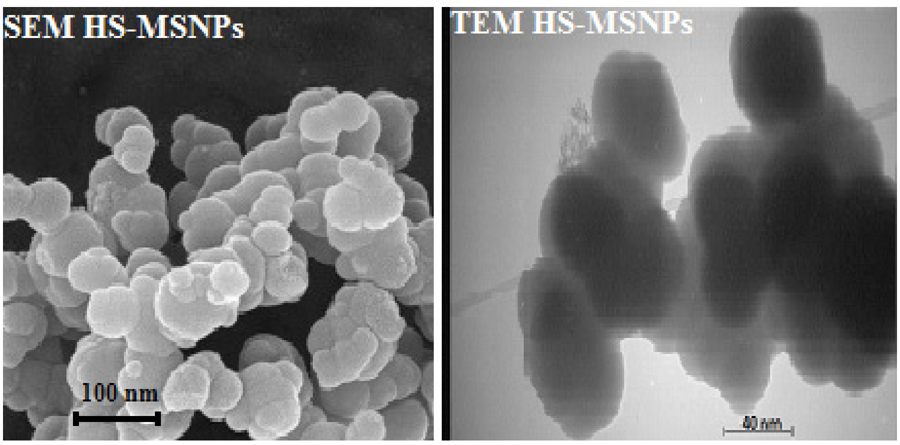

Fig. 1. (a)SEM of HS-MSNPs and (b) TEM of HS-MSNPs

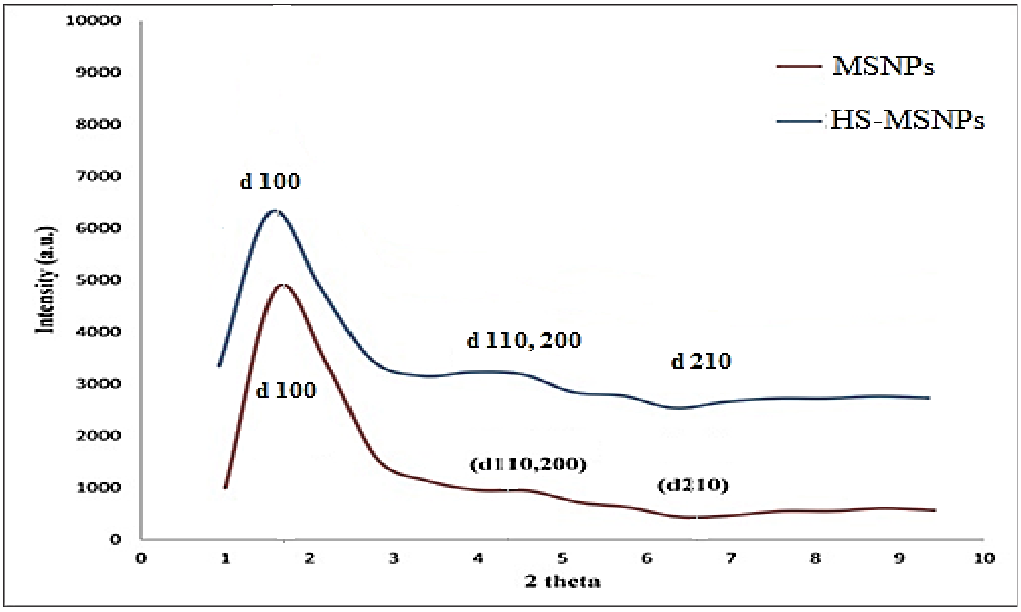

Fig. 2. The XRD of HS-MSNPs

as HS-MSNPs material were analyzed by FTIR in Waveland between 300 cm^{-1} to 4000 cm^{-1} (Fig. 3). The HS band was showed in Waveland of 2500 cm^{-1} (Germany).

2.4. General procedure

The packed column micro solid phase extraction (PC-MSPE) was used for separation and preconcentration of Pb(II) ions in human urine, standard solution and water samples. First, 5 mL of the lead standard solution containing 0.1 -5.5 µg L^{-1} as a LLOQ and ULOQ was used and pH adjusted up to 6. After optimized pH, the standard and urine samples directly transferred to in 5 mL of syringe cartridges with cellulose membrane which was already packed with 15 mg of HS-MSNPs and MSNPs as a sandwich form between membranes manually. The syringe cartridges (SC) included packed sorbent in cellulose membrane (PSCM) was used for extraction of Pb (II) from

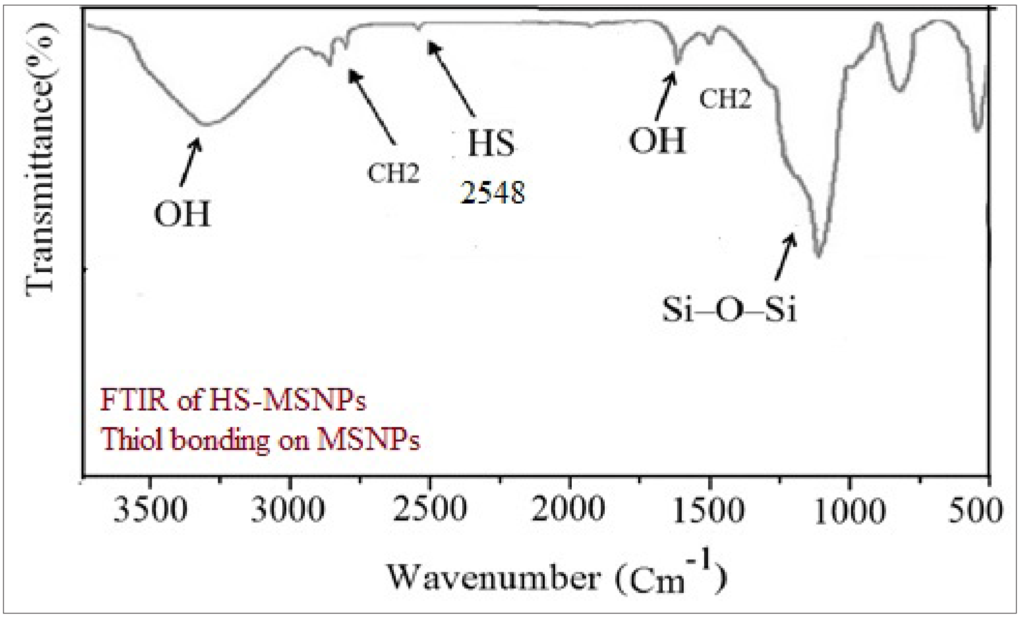

Fig. 3. FT-IR spectra patterns HS-MSNPs in 2500 cm^{-1}

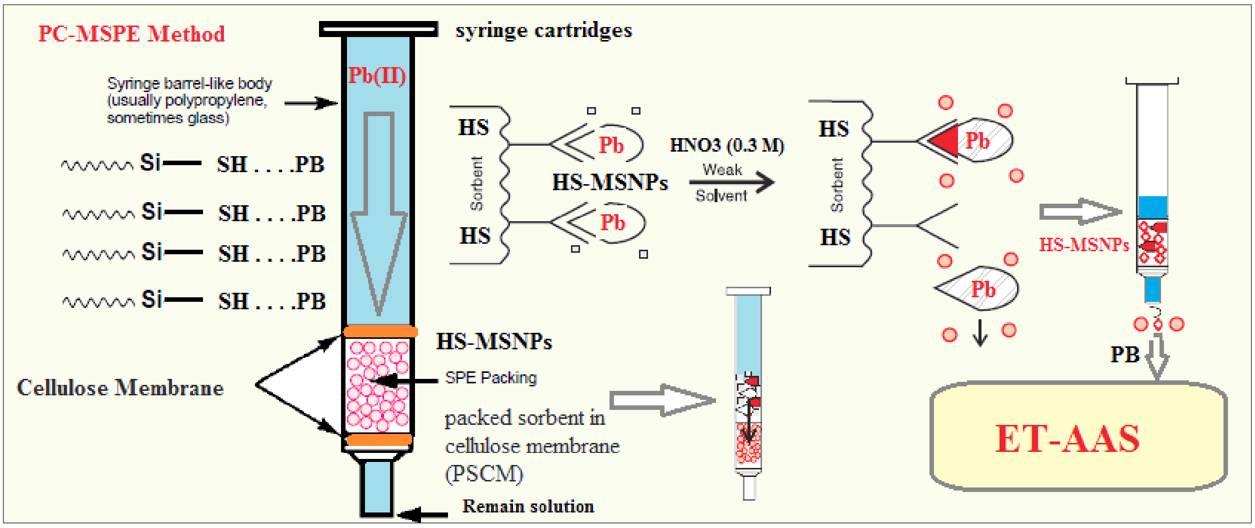

Fig. 4. The general procedure for lead extraction by PC-MSPE

liquid phase by PC-MSPE. Then the urine samples were fast extracted through PSCM of HS-MSNPs with pushing the plunger and the solid/liquid phases were separated. The Pb ions chemically and physically absorbed on HS-MSNPs. Finally, Pb(II) ions retained on the HS-MSNPs were eluted by passing 0.2 mL of nitric acid (0.3 ^{M}) through the SC and the lead value in the eluent was determined by ET-AAS (Fig. 4). The project approved by the ethical committee of K.U.M.S. (Ethical Code:IR.KMU.REC. 1398. 453)

3. Results and Discussion

3.1. The pH optimization

The pH is one of the most important parameters which were affected on lead extraction by PC-MSPE procedure. The effect of urine and standard pH on the extraction of Pb (II) by HS-MSNPs and MSNPs has investigated from pH of 1-12 containing 0.1-5.5 µg L^{-1} of lead ions by PC-MSPE method. Also, the extraction Pb ions in human urine sample were investigated in human pH. The results showed us, the extraction efficiencies of Pb (II) in urine samples were increased in pH from 5.5 to 6.5. The maximum recoveries were achieved in optimized pH (more than 97%) and decreased in 5.5 > pH > 6.5. So, the pH of 6.0 was selected as optimized pH for Pb extraction in urine and water samples. Furthermore, the Pb(II) and other metals was more extracted by extra mass (50 mg) of HS-MSNPs as physically adsorption simultaneity. In optimized conditions, the mean extraction of Pb was obtained less than 98.7% and 34.6% by 15 mg of HS-MSNPs and MSNPs, respectively at pH=6. The extraction mechanism of Pb ions on the HS-MSNPs is mainly based on the electrostatic attractions of deprotonated sulfur of thiol groups with the positively charged Pb ions.

3.2. The mass optimization

For optimization of proposed method, the amounts (mg) of HS-MSNPs and MSNPs in the range of 1 to 30 mg were studied for extraction of 0.1-5.5 µg L^{-1} of Pb(II) in human urine and water samples. The results showed us, more than 12.5 mg of HS-MSNPs had good extraction recovery for Pb(II) in standard samples. So, 15 mg of HS-MSNPs was used as optimized amount of HS-MSNPs by PC-MSPE method (Fig. 6). More than 15 mg of HS-MSNPs got no significant extraction on the recovery of lead urine and water samples. For 15 mg of MSNPs, the extraction recovery was obtained less than 35% at pH=6 and was increased up to 44.4 % at pH=3.

3. 3. The sample volume optimization

The sample volume effected on the recovery of Pb(II) ions based on PC-MSPE in standard and human urine samples. So, the sample volume was evaluated from 1-20 mL in optimized conditions.

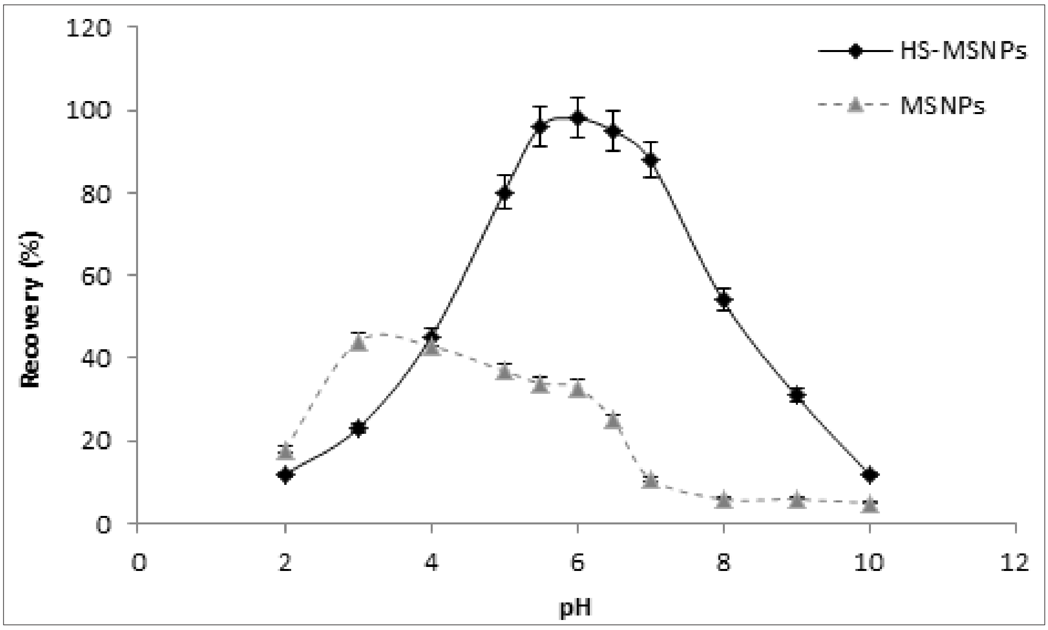

Fig. 5. The effect of pH on lead extraction by HS-MSNPs and MSNPs

The results showed us, the quantitative extraction was achieved less than 5 mL sample by 0.1 – 2.5 µg L^{-1} of Pb as LLOQ and ULOQ range (≈97%). The extraction recovery was reduced more than 8 m and 10 mL of sample volume for urine and standard/water samples, respectively. As normal range of Pb in urine and waters (TLVs) a syringe cartridges (SC) of 5 mL were used for urine and water samples (Fig. 7).

3. 4. Adsorption capacity and separation time

In the batch system, the adsorption capacity (AC) of HS-MSNPs and MSNPs for lead extraction was calculated by ET-AAS. The adsorption capacity of Pb (II) was investigated for 5 mL of human urine sample and standard solution at pH=6 (15 mg HS-MSNPs and MSNPs). The pH was adjusted by using buffer solution and after shaking of SC, lead ions chemically and physically absorbed on sorbents. The residual solutions were determined

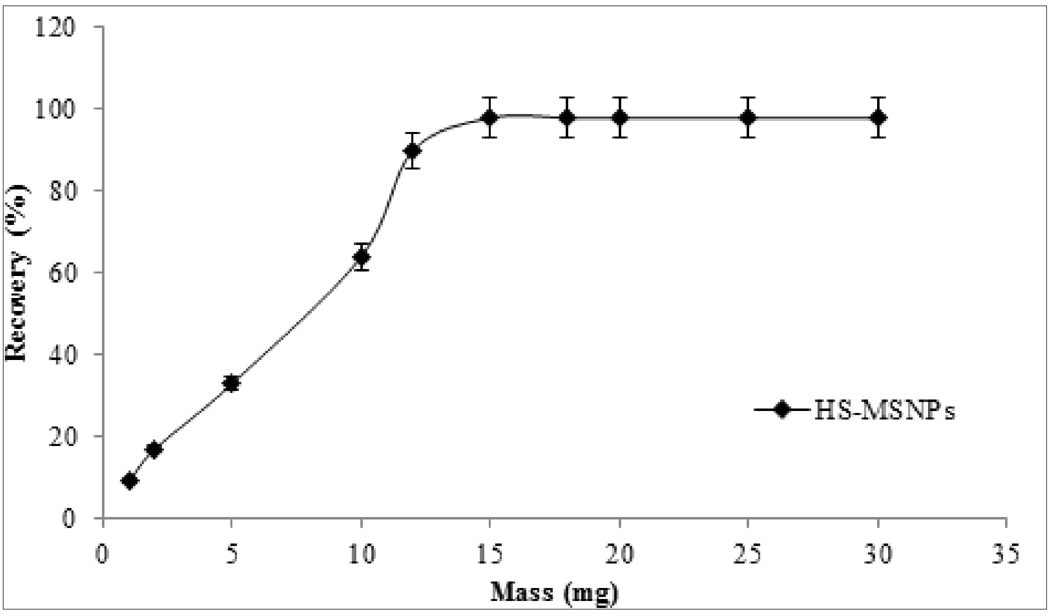

Fig. 6. The effect of mass of HS-MSNP on lead extraction by PC-MSPE method

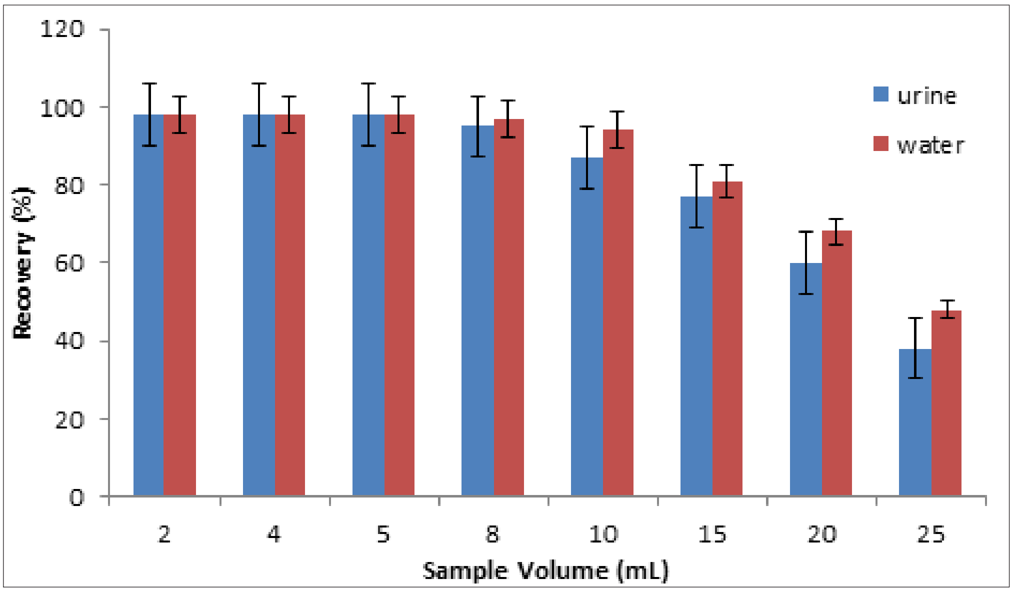

Fig. 7. The effect sample volume on lead extraction in water and urine samples

by ET-AAS. The adsorption capacity of HS-MSNPs and MSNPs for Pb ions was 186.3 mg g^{-1} and 64.8 mg g^{-1}, respectively. The results showed, the recovery of HS-MSNPs was higher than MSNPs as characterization and chemical bonding. So, the HS-MSNPs were used as excellent sorbent for extraction of Pb (II) in this study. Also separation time for extraction of lead ions was investigated between 2 min to 10 min. The result showed that, 4.5 min was an optimum time for excellent recovery. This time was controlled by pushing the plunger.

3. 5. Back extraction process

The maximum recovery for lead extraction was carried out in optimum conditions. The lead was back extracted from HS-MSNPs by different concentration of inorganic and organic acids such as HNO_3, HCl, CH_3COOH and H_2SO_4. The chemical adsorption between HS-MSNPs and Pb ions was dissociated at acidic pH. For optimizing, 0.1-0.5 mL of acids with different concentration from 0.1- 0.5 mol L^{-1} was studied. Based on results, 0.2 mL of HNO_3 (0.3 mol L^{-1}) had good recovery (Fig. 8).

3. 6. Interference study

By PC-MSPE method, the interference of coexisting ions (cations and anions)such as; SO_4^{2-}, Cl^-, Br^-, NO_3^-, CO_3^{2-}, Cd^{2+}, AS^{3+}, Hg^{2+}, Ag^+, Co^{2+}, CU^{2+}, Zn^{2+},Mn^{2+}, V^{3+}, Al^{3+} and Ni^{2+} in water and urine samples was studied. So, different concentration of coexisting ions (1—5 mg L^{-1}) was added to 5 mL of standard sample solution with lead concentration of 5.5 μg L^{-1}. Based on results, the most concomitant ions cannot effect on extraction of Pb in samples. The mean of concentration ratio of above coexisting ions per lead was less than 500. Therefore, the Pb ions in urine samples were efficiently extracted with HS-MSNPs in present of coexisting ions (less than 5%).

3.7. Discussion

Mortada et al investigated the pre-concentration of Pb^{2+} from blood and urine samples with mesoporous strontium titanate nanoparticles and determined the samples by FAAS. The characterization was obtained by FT-IR, XRD, SEM-EDX, and TEM. In optimized conditions, the pH, shaking time, mass sorbent and adsorption capacity was achieved at 6, 20 min, 50 mg and 155.6 mg g^{-1} which was lower than PC-MSPE procedure in this study. The limit of detection and relative standard deviation was 1.75 μg L^{-1} and 2.5%, respectively which was higher than our proposed method by HS-MSNPs (LOD=0.04 μg L^{-1}, 2.2 %)[44]. In another research,

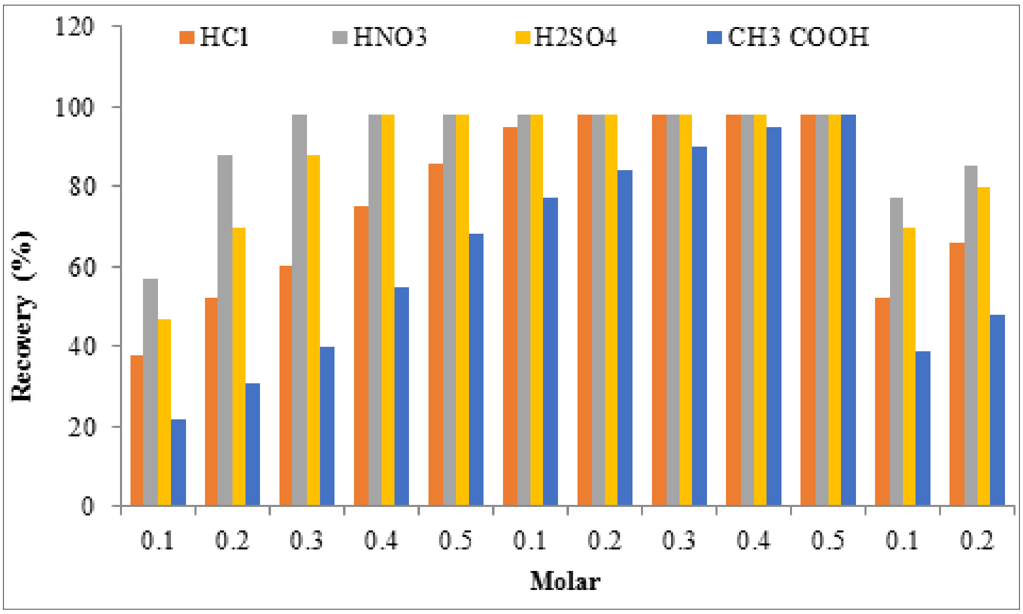

Fig. 8. The effect acids on lead extraction with HS-MSNPs

Behbahani et al used the method of solvent-assisted dispersive solid-phase extraction (SA-DSPE) to determine lead in fruit and water samples. After lead extraction the samples was determined by flame atomic absorption spectrophotometer (F-AAS). Based on results, LOD =1.2 µg L^{-1} was obtained as compared to lower LOD (0.04 µg L^{-1}) by PC-MSPE method [45]. Kakavandi et al, reported ultrasonic assisted-dispersive solid-phase extraction based on ion-imprinted polymer (UA-DSPE-IIP) nanoparticles as a selective extraction for lead ions. Box-Behnken design (BBD) was used for the optimization of sorption and desorption steps in UA-DSPE-IIP. Under the optimized conditions, the limit of detection and relative standard deviation for the detection of lead ions by UA-DSPE-IIP was found to be 0.7 µg L−1 and <4%, respectively which was higher than proposed method based on HS-MSNPs by PC-MSPE method [46]. Also, a magnetic sorbent (MoS2-Fe3O4) based on dispersive solid-phase microextraction (DSPME) was used for separation Pb(II) and copper(II) ions from water samples by Soylak. LODs and RSD of 3.3 µg·L^{-1}, 4.9 for Pb(II) and of 1.8 µg·L^{-1}, 1.5% for Cu(II), was achieved by F-AAS. So, PC-MSPE method had better results as compared to MoS2-Fe3O4 sorbent [47]. Jiamei at al showed mesoporous silica-grafted graphene oxide (GO-SBA-15) as sorbent and packed it in an SPE microcolumn with solution-cathode glow discharge-atomic emission spectrometry (SCGD-AES) method. The detection limit (DL) of Pb(II) was calculated to be 0.91 µg L− 1 which was higher than PC-MSPE procedure [48]. Shahad et al used mesoporous silica with nanospheres as a substrate and the organic ligand of 2,5-di mercapto-1,3,4-thiadiazole, for lead removal from wastewater with LOD of 0.48 µg L^{-1} and adsorption capacity of 67.20 mg g^{-1}[49]. sobhi et al suggested ultrasonic-assisted dispersive micro-solid phase extraction (d-µSPE) method with GF-AAS for measuring of lead in water and urine samples by silica-based amino-tagged nano sorbent (MCM-41@NH2. The result showed that linear range, RSD and recovery was obtained 0.1–1.0 µg L^{-1}, 4.8–9.2% and 92–110%, respectively. The wide linear range and lower RSD was achieved for PC-MSPE as compared to d-µSPE method [50]. Amiri et al synthesized magnetic natural clinoptilolite (CP for simultaneous determination of lead (II) and cadmium (II) ions by FAAS. The limit of detection (LOD) using this method were found to be 0.93[51]. Raoof et al use the graphene oxide-soluble eggshell membrane protein (GO-SEP) by inductively coupled plasma-optical emission spectrometry (ICP-OES). The GO-SEP-ICP-OES with LOD of 0.1 μg.L^{-1} was equal to PC-MSPE method [52]. Baile et al used magnetic dispersive solid-phase microextraction (MDSPME) method, based on ZSM-5 zeolite decorated with iron oxide magnetic nanoparticles (*i.e.*, ZSM-5/Fe2O3) for the simultaneous separation and preconcentration of cadmium (Cd), mercury (Hg) and lead (Pb) from urine [53].

3.8. Validation of procedure

A novel method based on HS-MSNPs was applied for lead extraction for 5 mL of urine and water samples by PC-MSPE. For validation, real samples (water and urine) were spiked by standard lead samples in different concentration from LLOQ to ULOQ. The method was approved with good precision and accuracy results with low RSD% (Table 1). Also, the proposed method was validated by power instrumental analysis (ICP-MS) as compared to PC-MSPE procedure (Table 2). The certified reference material (CRM, NIST) in water and wastewater samples were used for validating of results by PC-MSPE method. Experimental results of the CRM sample were satisfactorily confirmed the certified values of lead (Table 3). The recoveries of spiked water and urine samples

Table 1. Validation of PC-MSPE method based on spike of lead standard concentration

Sample	Added (μg L^{-1})	*Found(μg L^{-1})	Recovery%
Urine A	------	2.34 ± 0.09	------
	2.0	4.28 ± 0.17	97
Urine B	------	1.02± 0.04	------
	1.0	1.97± 0.11	95
Well Water	------	0.46 ± 0.02	------
	0.5	0.97± 0.05	102
[a] **Wastewater**	------	2.16 ± 0.12	------
	2.0	4.14± 0.18	99

[*] Mean of three determinations ± confidence interval (P = 0.95, n =10).

[a] Wastewater samples was diluted with DW (1:20)

Table 2. Comparing of PC-MSPE method with ICPMS for lead determination

Sample	Added	ICP-MS	PC-MSPE	ICP-MS Recovery%	PC-MSPE Recovery%
Urine	------	1.82 ± 0.04	1.78 ± 0.09	------	------
	2.0	3.79 ± 0.05	3.69 ± 0.21	98.5	95.5
Water	------	0.73 ± 0.02	0..68 ± 0.03	------	------
	0.5	1.21± 0.03	1.19 ± 0.05	96.0	102.0

* Mean of three determinations ± confidence interval (P = 0.95, n =10).

Table 3. Validation methodology by Sigma CRM and ICP-MS for PC-MSPE method

CRM sample	ICP-MS	CRM (μg/L)	*Found(μg L^{-1})	Recovery%
*ERMCA713	4.92 ± 0.12	4.97 ± 0.17	4.88 ± 2.4	98.2
1640a	1.19 ± 0.02	1.21 ± 0.02	1.23± 0.06	101.6
Urine	2.07 ± 0.09	------	1.98 ± 0.09	95.6
Drinking water	0.51± 0.01	------	0.49± 0.03	96.2

*Mean of three determinations ± confidence interval (P = 0.95, n =10)

[a] Sigma Aldrich, Cat. No. ERMCA713, lead in wastewater diluted up to 10.

[b] NIST SRM 1640a, lead in water, diluted up to 10.

for Pb(II) were ranged from 95% to 102%, which demonstrated that the PC-MSPE method was satisfactory extracted and determined Pb ions in human urine samples (n=10).

4. Conclusions

The simple, applied and reliable SPE technique for determination of trace levels of Pb (II) ions in real water and urine samples was developed based on HS-MSNPs by ET-AAS. The PC-MSPE method provided good recoveries (>95%) in optimized conditions. By procedure, reproducibility and reliability data with low RSD (under 5%) in 10 experiments were obtained. The batch adsorption capacities of lead on MSNPs and HS-MSNPs were found to be 64.8 and 186.3 mg g^{-1}, respectively. The PC-MSPE procedure has some advantages such as, excellent separation, high surface area, low consumption of only 15 mg of HS-MSNPs, good enrichment factor for 5 mL of sample, only 0.2 mL of eluent per extraction, high absorption capacities, low LOD, and favorite reusability (more than 20). It is expected that the PC-MSPE procedure based on nanotechnology could successfully be extracted lead ions from urine and water samples.

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