A novel method based on functionalized bimodal mesoporous silica nanoparticles for efficient removal of lead aerosols pollution from air by solid-liquid gas-phase extraction

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Abstract

In this study, the enrichment and novel sorbent based on functionalized bimodal mesoporous silica nanoparticles (HS-UVM₇ and NH₂-UVM₇) was used for removal of lead aerosols pollution from air by solid liquid gas phase extraction method (SLGPE). In bench scale set up, the lead aerosols [(Pb(NO₃)₂, PbO)] was generated by dispersive aerosols generator system (DAGS) and removed from air by reaction loop (RL) / impinger trap (IT) in a liquid phase which was mixed with nano adsorbent in optimized pH. The effect of parameters such as, flow rate, volume of liquid phase, time stirring, temperature, concentration, pH and amount of sorbent (mg) were studied and evaluated by flame atomic absorption spectrometry (FAAS). In optimized conditions, the adsorption capacity of HS-UVM₇ and NH₂-UVM₇ for Pb(NO₃)₂ aerosols was obtained 255.6 mg g⁻¹ and 177.6 mg g⁻¹, respectively which was more than UVM₇. The lead oxides aerosols (PbO) were extracted only by HS-UVM₇ at acidic pH with the adsorption capacity of 271.2 mg g⁻¹. The characterization of SEM, XRD, TEM, and FTIR showed that the HS-UVM₇ has beneficial surfaces for removal of (Pb(NO₃)₂ and PbO aerosols from the air by SLGPE method at pH = 5. The method validation was confirmed by standard addition and NIOSH method.

Keywords Lead aerosols removal · Air pollution · Functionalized bimodal mesoporous silica nanoparticles · Solid liquid gas phase extraction · Aerosols generator system

Introduction

For many years ago, the heavy metals have been used in industries by human activity. Also, the toxic effects of heavy metals on human health have been considered in different countries by WHO [1–3]. These chemical elements of the earth's crust cannot degrade or change to a simpler form. Moreover, the heavy metals can be conveyed to human bodies

by air, water, and agricultural products [4, 5]. Human exposure to toxic metals can occur in different origins including, industries activity (dust, fume, and wastewater) environment (air, water, soil) and foods. A lot of heavy metals are released from mines, oil companies and chemical factories. Also, the exposure to toxic metals (Pb, hg, as, Mn, Al) is dangerous for human health due to the combustion of leaded gasoline. Many metal aerosols and gas pollutants created from crude oil and must be removed from oil before enter to air [6, 7]. Moreover, sometimes, the heavy metals generate by recycled products such as battery factories [8, 9] and high exposure in air threatens people's health. In some developed countries, field-portable tools are used for protecting workers from airborne metals [10]. The lead (Pb) is used as an additive to petrol, building materials, and pipes and can be released in waters. In addition, Lead emissions due to the combustion of petrol have polluted ambient air and caused a lot of widespread diseases. Moreover, every day, a lot of metal aerosols convey from one place to another by air and water. Airborne lead set down on soil, air and water and enters to human body

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from food chain or breathing up to 10–15% and 50% in adults, respectively. In other hands, the lead absorb by gastrointestinal of children up to 50% [3]. The aerosols, metals and VOCs were studied in several fields, including epidemiology, respiratory medicine, air purification technology, and air pollution removal by different techniques and pilots [11–14]. Aerosols are further categorized on the basis of the variation in the particle size. Aerosols with broad particle size distribution are known as poly-disperse aerosols. Aerosols with narrow particles size distribution are called monodisperse aerosols. Dispersion, condensation and dispersal of powders is important part of aerosol technology [15]. Lead can enter to blood serum and erythrocytes (half-life of 1 month) from digestion and respiratory system and then move to the skeleton tissue (half-life of 20 years) and finally, eliminate by urine [16]. The more information was shown in text S1 of electronic supplementary material (ESM). The sample preparation of metals in liquid phase flowed by liquid-liquid extraction (LLE), but in air/gas, sorbents as a solid phase was used for removal of metals or other materials. In liquid phase, solid phase extraction (SPE) was selected as a favorite technique for removal of heavy metals or volatile organic compounds (VOCs) [17, 18]. In optimized conditions by SPE, the appropriate sorbent is an important factor for efficient extraction and recovery. Many sorbents such as graphene, activated carbon, silica gel, titanium dioxide, resins and CNTs have been used for removal of gases, organic compounds and metal ions [19]. The mesoporous siliceous nano material (MSN) increased the applications potential in catalysis, separation techniques, controlled delivery, sensors, isolation, concentration, clean-up, optical devices, etc. [20]. Based on previous study, three classes of porous materials (PM) included, microPM, mesoPM, and macroPM was used as adsorbent for extraction or removal of materials in different matrixes [21, 22]. Mesoporous silicate materials (MSM) with wide surface area and tuneable pore size were used as a high efficient adsorbent for extraction process which facilitate the diffusion of large amount of analyte inside the pores [18]. The functional groups of MSM ($R = OH, CN, S, NH_2$) increases the adsorption capacity of sorbent based on chemical adsorption properties [23]. A new form of MSM is MSN with higher surface area and physical adsorption [21]. The MSN was used in sorbent catalyst, separation process, optical condition and biomedical technology [24]. These nanomaterials are used for water treatment by adsorption of heavy metal [25]. The bimodal mesoporous silica nanoparticles (UVM₇) can be considered as a version of the MSM or MSN [26, 27]. In this work, lead aerosols were removed from air based on HS-UVM₇/NH₂-UVM₇/UVM₇ nanoparticles by SLGPE technique before determined by F-AAS. By SLGPE method, HS-UVM₇/NH₂-UVM₇/UVM₇ as an adsorbent was compared and validated with XRD/mixed cellulose ester membrane (MCEM) for analyzing of lead particles in air by NIOSH method (NIOSH 7702). By DAGS, the

experimental parameters affecting on removal of *pollutant lead aerosols* from air were studied and optimized. The lead concentration in air was calculated based on lead concentration in liquid phase which was depended to extraction time, temperature, and flow rate

Material and method

Apparatus and reagents

The analytical grade of reagents such as, sodium oxide, sulfuric acid, nitric acid, hydrochloric acid (HCl), acetic acid (CH₃COOH), tetraethoxysilane (TEOS, N: 800–6,580,025), tri-ethanol amine (TEAH₃, N: 102–71-6), Cetrimonium bromide (CTAB, N: 57–09-0), sodium hydroxide, lead nitrate salt (CAS number: 10099–74-8), lead oxide powder and 3-mercaptopropyltriethoxysilane (C₉H₂₂SO₃Si) were purchased from Sigma Aldrich (Darmstadt, Germany). The sodium silicate (N: SX0755, NIST traceable, Sigma Germany), ethanol (96 wt.%), and toluene were prepared from Merck (Germany). The standard solution of Pb(II) was prepared from the lead salt by solvation in DW as 1 g L⁻¹ concentration in nitric acid 2% (Pb (NO₃)₂). The different concentration of Pb (NO₃)₂ were prepared daily by dilution of the stock solution in nitric acid. In order to show the purity of HS-UVM₇ / NH₂-UVM₇ as adsorbents, F-AAS was used for determination of metal concentration in adsorbent. The impulse mixing polyethylene bag was purchased for storage air with five port (IMPBC, 0.5–5 Li, ASI certified manufacturer, USA, Cas N: PL-01026 / PL-01077).

The more information was shown in text S2 of electronic supplementary material (ESM).

Synthesis of thiol and amine functionalized on UVM₇

The synthesis of UVM₇ was obtained in presence of the poly-alcohol for hydrolysis and reaction rates. The more information for synthesis of UVM₇ was shown in text S3 (ESM). For amine functionalization of UVM₇, 3.0 g of triethoxysililpropylamine (C₉H₂₃NO₃Si) and 5 g of UVM₇ was added to amount of toluene for 72 h at 70 °C. The NH₂-UVM₇ were dried at 80 °C over night at room temperature. For thiol functionalization of calcined UVM₇, 1.4 g of 3-mercaptopropyltriethoxysilane (C₉H₂₂SO₃Si) and 1.5 g of calcined UVM₇ in presence of toluene, were refluxed for 24 h and then washed with DW. Finally, the HS-UVM₇ was dried at 348 K overnight.

Characterizations

Functional groups of NH₂ and SH on UVM₇ were analyzed by Fourier transform infrared spectrophotometer (FTIR, IFS

88, Germany) in the 5000–250 cm^{-1} . The adsorption capacity of lead aerosols for the thiol and amine functionalized UVM₇ was evaluated by determining the concentration of lead in the liquid phase by UV–Vis spectra from 200 nm to 800 nm. The more information of characterization of UVM such as, X-ray diffraction (XRD) patterns, textural properties of the sorbent by nitrogen isotherms, specific surface areas, the BET surface area of UVM-7, NH₂-UVM-7 and HS-UVM-7, was shown in text S4 and fig. S1 (ESM).

General procedure

The efficient removal of *lead aerosols* [$\text{Pb}(\text{NO}_3)_2$, PbO] was evaluated in present of pure air in different flow rate by HS-UVM₇ / NH₂-UVM₇ and UVM₇ adsorbents. The procedure was used in static and dynamic system in optimized conditions by dispersive aerosols generator system (DAGS). The air was purified with electro air cleaner (EAC, Canada, model EAHEPA600M-3) by HEPA. It acts to remove of particles size from 200 nm to 300 nm (more than 95%). Then, the pure air of EAC entered to DAGS by polyethylene tubes (50–300 mL min^{-1}). By proposed pilot, the pure air without lead aerosols was determined as a blank air ($n = 10$) by F-AAS and validated by ET-AAS. In addition, XRD/mixed cellulose ester membrane (MCEM) was used for analyzing of lead particles in air by NIOSH method and compared to SLGPE procedure in dynamic system.

Static and dynamic procedure

For static procedure, the polyethylene bags based on recirculation pump and five ports included, liquid addition, recirculation, air aerosols inlet and vent air control were used (1.5 Li, IMPBC). The tube of IMPBC sets are modular and can be customized to best suit proposed process. 10 mg of HS-UVM₇, NH₂-UVM₇ and UVM₇ was dispersed in 100 mL of liquid phase (DW) and entered from liquid port of IMPBC bag in different pH = 5, pH = 7 and pH = 3, respectively. Then, the 30 mg of lead aerosol [$\text{Pb}(\text{NO}_3)_2$, PbO] dissolved in NaOH/DW and sprayed into chamber (1 Li) by nebulizer of dispersive aerosols generator system (DAGS). After drying up to 120 °C, lead particles of Pb (NO_3)₂ and PbO were moved with pure air (100 mL min^{-1}) to air port of IMBC bag for 10 min (Stock lead aerosol:1 Li). After recirculation of solution in IMPBC bag for 60 min (shaking), the liquid was vacuumed from bag and sorbent separated from liquid phase with centrifuging. The back extraction of lead from sorbent was obtained in acidic pH (HNO₃, 0.5 M, 10 mL). After dilution with DW, the lead concentrations were determined by F-AAS. In optimized conditions, the adsorption capacity of 177.6 mg g^{-1} and 265.6 mg g^{-1} was obtained for Pb(NO_3)₂ with 10 mg of NH₂-UVM₇ and HS-UVM₇, respectively. The adsorption capacity of 9.5 mg g^{-1} and

25.4 mg g^{-1} was obtained for 10 mg of UVM₇ in pH = 7 and pH = 3, respectively. The more information for static procedure was shown in text S5_a and fig. S1 (ESM).

In dynamic procedure, the lead removed from air by solid liquid gas phase extraction method (SLGPE). The bench scale was designed as follows, the column length (30 cm) with center glass (Pore 5) in bottom of glassy container for air bobbles, SKC pump with air flow rate 50–300 L min^{-1} , DW with pH = 3–7, 10 mg of nano particles of HS-UVM₇, NH₂-UVM₇ and UVM₇ which was dispersed in solution (Fig. 1). 0.2 mg per mL of Pb(NO_3)₂ and PbO as a stock lead solution spray in chamber (1Li) and flowed with pure air with different flow rate from 40 to 500 ml min^{-1} . The lead aerosols was prepared by pilot and moved to mixer with flow rate 100 mL min^{-1} (port 1). 10 mg of HS-UVM₇, NH₂-UVM₇ or UVM₇ as a nano-sorbent was dispersed in 100 mL of liquid phase in glassy container (150 mL) at optimized pH. The mixture of sorbent in liquid phase moved to mixer (port 2) through peristaltic pump, the liquid phase and air aerosols mixed in U-reaction loop (polyethylene tube) and then back stored in glassy container (pore size 5) with magnet stirring for 10 min. After stirring solution, the sorbent separated from liquid phase and lead was back extracted by acid solution (0.5 M, 10 mL). Finally, the remained solution was determined by F-AAS. In addition, the adsorption capacity of sorbents for dynamic system is lower than batch system for 10 mg of different sorbents (pH = 5 for HS-UVM₇ and pH = 7 for NH₂-UVM₇). The results showed us, the Pb(NO_3)₂ aerosol was removal by HS-UVM₇ and NH₂-UVM₇ in optimized pH and PbO aerosol only removal by HS-UVM₇ at pH = 5. So, HS-UVM₇ was selected as suitable sorbent with high removal efficiency of pollutant lead aerosols by SLGPE method. The more information for dynamic procedure was shown in text S5_b (ESM).

Results and discussion

Mechanism of removal

In optimized pH, the strong interactions between thiol and amine group of UVM₇ and lead aerosols in liquid phase caused to remove lead aerosols from air based on HS-UVM₇ and NH₂-UVM₇ by liquid gas phase extraction in all layers. The interaction between gas and liquid phase was depended to solubility of lead aerosol in liquid phase at optimized pH, temperature and flow rate which was increased by functionalized thiol and amine group on UVM₇. By converting of lead aerosols to lead ions in liquid phase, the extraction mechanism of Pb (II) ions on the HS-UVM₇ and NH₂-UVM₇ was demonstrated based on the complex formation between cations of Pb (II) and sulfur/amine groups of UVM₇, which is strongly

Fig. 1 The dynamic system for removal of lead nitrate and oxide aerosols from air

dependent on pH range (Fig. 2). The more information was explained in text S6 (ESM).

XRD analysis

Three diffraction peaks was seen in XRD patterns of UVM₇, HS-MSN and NH₂-UVM₇. The hexagonal symmetry peaks can be indexed as the (100), (110), (200) and (210) which d_{110} and d_{200} peaks were overlapped with each other. The XRD

patterns of UVM₇, HS-UVM₇ and NH₂-UVM₇ are shown in fig. S3. The more information for XRD patterns was shown in text S7 (ESM).

Specific surface area

The specific surface area (S_{BET}) of UVM₇, HS-UVM₇ and NH₂-UVM₇ were obtained 865 m² g⁻¹, 547 m² g⁻¹ and 624 m² g⁻¹, respectively. The decreasing of BET surface

Fig. 2 Mechanism of removal of lead aerosol from air based on NH₂/HS-UVM₇ by SLGPE

Table 1 Textural properties of UVM₇, HS-UVM₇ and NH₂-UVM₇

Sample	$S_{\text{BET}}^{\text{a}}$ (m ² /g)	d_{sp}^{b} (nm)	d_{lp}^{c} (nm)	V_{sp}^{d} (cm ³ /g)	V_{lp}^{e} (cm ³ /g)	a^{f} (nm)	W_{t}^{g} (nm)
UVM ₇	865	2.68	52.5	0.43	0.82	5.59	2.92
HS-UVM ₇	547	2.59	37.8	0.25	0.38	5.59	3.01
NH ₂ -UVM ₇	624	2.63	42.4	0.28	0.42	5.59	2.97

^a BET specific surface area, ^b diameter of small pores, ^c diameter of large pores, ^d Volume of small pores, ^e Volume of large pores, ^f Unit cell parameter obtained from XRD diffractograms ($2d_{100}/\sqrt{3}$), ^g Wall thickness(nm) obtained by following equation: $W_{\text{t}} = a - (d_{\text{p}}/1.05)$

area of HS-UVM₇ and NH₂-UVM₇ as compared to UVM₇ are due to the grafting of HS or NH₂ on walls. Textural properties of UVM₇, HS-UVM₇ and NH₂-UVM₇ were calculated and presented in Table 1. The more was shown in text S8 (ESM).

Elemental analysis, SEM and TEM imaging

The more information for elemental analysis was shown in text S9 (ESM). The SEM and TEM of HS-UVM₇ and NH₂-UVM₇ showed a similar morphology and particle size distribution (Fig. 3a, b). The more information was shown in text S10 of ESM

FT-IR analysis

The fig. S4 (a) and S4(b) indicates the FT-IR spectra patterns of UVM₇ and NH₂-UVM₇ and HS-UVM₇ in the range of 3500–500 cm⁻¹. Based on results, the presences of amine and thiol group in UVM₇ were confirmed. The more information of FTIR was shown in text S11 of ESM.

Effect of pH

Lead oxide and nitrate aerosols convert to Pb²⁺ in liquid phase, the Pb²⁺ ions in liquid phase adsorbed on NH₂-UVM₇ or HS-UVM₇ surface with chemically reacting by NH₂⁻/HS⁻

Fig. 3 **a** The SEM of NH₂-UVM₇ (N) and HS-UVM₇ (S), **b** The TEM of NH₂-UVM₇ (N) and HS-UVM₇ (S)

groups in optimized conditions. Depending on the solution pH, the surfaces of the $\text{NH}_2\text{-UVM}_7$ / HS-UVM_7 can undergo protonation or deprotonation reaction. Surface charge of the $\text{NH}_2\text{-UVM}_7$ / HS-UVM_7 is negative charge due to the deprotonation reaction at optimized pH. As a result of electrostatic force, Pb^{2+} ions extracted by negative functional groups (Eq. 1, lead nitrate aerosols).

- a) $n(\text{NH}_2\text{-UVM}_7) + n(\text{OH})^- \rightarrow n[\text{UVM}_7\text{-NH}_2^-] - - - \text{Pb}^{2+}$
 pH = 7 (Eq. 1, $\text{Pb}(\text{NO}_3)_2$)
- b) $n(\text{HS-UVM}_7) + n(\text{H})^+ \rightarrow n[\text{UVM}_7\text{-HS}^-] - - - \text{Pb}^{2+}$
 pH = 5

In the SLGPE method, the lead particles in aerosols enter to liquid phase and convert to ions in optimized pH (lead nitrate: pH = 3–7; lead oxide: pH = 3–5) then, the appropriate interaction between sorbent and analyte were existed. The pH of solution is an important factor to obtain efficient conversion of air particles to ions in liquid phase and quantitative extraction of lead ions in liquid phase by surface charge of the adsorbent or function group. So, the influence of pH on the extraction recovery of lead was studied in pH of 2–10 (0.2 mg L^{-1} of lead aerosol). The results showed us the solubility of lead oxide and lead nitrate aerosols in liquid phase was increased in acidic pH (3–5) and pH from 3 to 7, respectively. In addition, the extraction lead ions in liquid phase by $\text{NH}_2\text{-UVM}_7$, HS-UVM_7 and UVM_7 depended to pH (Fig. 4a, b and c). At low pH the thiol group has negatively charged and adsorption process between negative charges of SH group of HS-UVM_7 with positive charge of Pb was achieved at pH = 5. Based on Fig. 4, in acidic pH up to 5, lead oxide aerosols convert to ions in liquid phase with positive charge and the removal efficiency increased more than 95% by HS-UVM_7 . After pH > 8, the recovery of Pb (II) ions was precipitated as a lead hydroxide $[\text{Pb}(\text{OH})_2]$. So, the optimized pH was used for further study (Eq. 2, pH = 5).

- a) $n(\text{NH}_2\text{-UVM}_7) + n(\text{H})^+ \rightarrow n[\text{UVM}_7\text{-NH}_2^+] \text{ Not bonding}$
 pH = 5 (Eq. 2, PbO)
- b) $n(\text{HS-UVM}_7) + n(\text{H})^+ \rightarrow n[\text{UVM}_7\text{-HS}^-] - - - \text{Pb}^{2+}$
 pH = 5

In varying pH, the recovery and absorption capacity of sorbents for lead nitrate and oxide aerosols was investigated (Fig. 4a, b and c). The lead nitrate aerosols convert to ions in liquid phase with positive charge at wide pH from 3 to 7 and the removal efficiency were obtained more than 95% and less than 60% by HS-UVM_7 (pH = 5) and $\text{NH}_2\text{-UVM}_7$ (pH = 7). So, the pH of 5 selected as optimum pH for extraction of lead nitrate and oxide aerosols from liquid phase by HS-UVM_7 . The results showed us the $\text{NH}_2\text{-UVM}_7$ cannot efficient extracted lead oxide

aerosols in liquid phase from air. The more information about pH was shown in text S12 of ESM.

Effect of the adsorbent mass and reusability

The extraction efficiency of lead ions with $\text{NH}_2\text{-UVM}_7$ and HS-UVM_7 were obtained more than 9 mg and 8.5 g, respectively (recovery more than 95%). So, 10 mg of $\text{NH}_2\text{-UVM}_7$ and HS-UVM_7 were used as the optimum adsorbent mass in liquid phase by SLGPE method. The more information was shown in text S13 of ESM.

In order to examine the long term stability of HS-UVM_7 , it was subjected to several extraction and elution cycles under the optimized conditions, according to the SLGPE procedures. The nanosorbent can be used for up to 32 adsorption–elution cycles (back extraction with nitric acid) without decrease in the extraction recoveries of lead.

Removal efficiency and adsorption capacity of sorbent

In this research, the removal efficiency and adsorption capacity of $\text{NH}_2\text{-UVM}_7$ and HS-UVM_7 in static system were studied. The important factors such as, temperatures ($25 - 80^\circ\text{C}$), flow rates (50, 100, 200 and 300 mL min^{-1}) and varying concentrations less than 30 mg L^{-1} (ppm) was researched. Finally, the adsorption capacity of 177.6 mg g^{-1} , 265.6 mg g^{-1} and 5.5 mg g^{-1} was obtained for lead nitrate aerosols with 10 mg $\text{NH}_2\text{-UVM}_7$, HS-UVM_7 and UVM_7 , respectively (Fig. 5a, b and c). The more information was shown in text S14 of ESM.

Effect of air and liquid flow rate

In this procedure, the effect of flow rate for lead aerosols removal from air was evaluated by SLGPE. In the suggested method, the varying flow rates between 50 to 600 mL min^{-1} were studied in liquid phase and air phase by DAGS. The flow rate of input and output of dynamic system was measured by a digital rotameter. The removal efficiency of lead and adsorption capacity of $\text{NH}_2\text{-UVM}_7$ / HS-UVM_7 was decreased in more than 120 mL min^{-1} . So, 100 mL min^{-1} of flow rate was selected as optimum flow rate in liquid and air phase for efficient removal of lead oxide and nitrate aerosols from air (Fig. 6a and b). The more information was shown in text S15 of ESM.

Method validation and column condition

Based on experimental results, the interaction between air and liquid phase was increased when the column designed correctly. The more information was shown in text S16 of ESM. In this method, the $\text{NH}_2\text{-UVM}_7$, HS-UVM_7 and

Fig. 4 **a** Effect of pH on recovery of lead nitrate by HS-UVM₇, NH₂-UVM₇ and UVM₇ **b** Effect of pH on recovery of lead oxide by HS-UVM₇, NH₂-UVM₇ and UVM₇ **c** Effect of pH on absorption capacity by HS-UVM₇, NH₂-UVM₇ and UVM₇

UVM₇ as sorbents was used for removal of lead aerosols (PbO and Pb(NO₃)₂) from air by solid liquid gas phase extraction method (SLGPE). For accuracy and precision of dynamic system, the lead concentration in DAGS was

determined by F-AAS and compared to proposed method. By proposed method, the lead aerosol with different concentration from 0.2 to 10 ppm was generated by DAGS and passed through dynamic system and removal from air.

Fig. 5 **a** The effect of temperature on removal efficiency of lead aerosols from air **b** The effect of mass of sorbent on removal efficiency of lead aerosols from air **c** The effect of initial concentration of lead aerosols on removal efficiency

All standard of lead aerosol was determined by high sensitive F-AAS. The standard reference material (SRM) for analysis of lead nitrate and oxide aerosol in air aren't available, so, the spiked of lead aerosol concentration (DAGS, 0.2–5 ppm, PE: 1 Li, 100 mL min⁻¹) were used

to method validation by NH₂-UVM₇, HS-UVM₇ and UVM₇ sorbents. At optimized conditions in 10 min, more than 95% of lead oxide and nitrate aerosols were almost removed from air by HS-UVM₇. The favorite results of spiked samples showed us the high potentials of NH₂-

Fig. 6 **a** The effects of different liquid flow rate / pH on the removal efficiency of lead aerosols **b** The effects of different air flow rate on the removal efficiency of lead aerosols

UVM₇, HS-UVM₇ for removal of lead from air. In other hands, the validation of proposed procedure was confirmed by standard addition. The results indicate the capability of NH₂-UVM₇, HS-UVM₇ for removal of lead air aerosols. After back extraction of lead from solid phase, the lead concentration was directly determined by F-AAS. Also, the method validation was obtained by ET-AAS (Tables 2, 3 and 4).

Comparing to other methods

The bimodal mesoporous silica nanoparticles (UVM₇) have more noted in many research by scientists because of special chemical properties and more applied applications. The different models of silica particles (MSNs, MSM and UVM₇) have many advantages in chemistry fields such as, low cost sorbent, efficient surface, nano metric size, high capacity and

Table 2 Method validation for HS-UVM₇ with spike of lead oxide in air

Sample*	DAGS (Conc. ppm)	FAAS (Conc. ppm)	Added (Conc. ppm)	Found (ppm) ^a	Recovery (%)
Sample A	0.2	0.2 ± 0.01	0.2	0.41 ± 0.02	105
Sample B	1.0	0.98 ± 0.06	0.5	1.46 ± 0.06	96.0
Sample C	2.0	1.93 ± 0.09	1.0	2.94 ± 0.12	101
Sample D	5.0	4.95 ± 0.23	2.5	7.42 ± 0.28	98.8
Sample E	7.5	7.46 ± 0.34	4.0	11.32 ± 0.41	96.5
Sample F	10.0	9.96 ± 0.37	5.0	14.83 ± 0.58	97.4

^a Mean of three determinations ± confidence interval ($P=0.95$, $n=5$)

* (Air bag; 0.2–10 ppm in 1 Li bag, 0.1 mL min⁻¹ air flow rate, Peak Area, 10 mg, T = 25 °C, pH = 5)

Table 3 Method validation of different sorbents with spike of lead nitrate in air

Sample*	DAGS (Conc. ppm)	pH	FAAS ^a (Conc. ppm)	Added (Conc. ppm)	Found ^a (Conc. ppm)	Recovery (%)
HS-UVM ₇	5.0	5.0	4.93 ± 0.25	5.0	9.86 ± 0.02	98.6
NH ₂ -UVM ₇	5.0	7.0	2.98 ± 0.16	5.0	5.89 ± 0.06	58.2
UVM ₇	5.0	3–5	0.93 ± 0.04	5.0	1.94 ± 0.12	20.2
AC	5.0	3–5	1.05 ± 0.23	5.0	2.21 ± 0.28	23.2
COOH-UVM ₇	5.0	7.0	2.93 ± 0.15	5.0	5.76 ± 0.41	56.6
Blank	5.0	5.0	ND	5.0	ND	–

^a Mean of three determinations ± confidence interval ($P = 0.95$, $n = 5$)

* (Air bag; 0.2–10 ppm in 1 Li bag, 0.1 mL min⁻¹ air flow rate, Peak Area, 10 mg, T = 25 °C, pH = 3–7)

adsorption of metals. The efficiency of UVM₇ have increased by function groups of thiol and amine on walls structure and increases the capacity and recovery [28]. The aerosol particles generated from different sources such as, environment, human activity, industries and factories. Some of particles like soils, dust wind, cars, wood firing, sea salts and volcanic materials are directly entered in air. The chemical composition of atmospheric aerosols (CCAA) especially particle material with micro size (PM: 2.5 M) have significant impact on human health and environment. So, CCAA removal from air is very important factor for human health. The removal of PbO and Pb (NO₃)₂ from air can be proceed by physical and chemical adsorption of sorbent. The previous study showed us the chemical bonding had more removal efficiency than physical adsorption such as filtration of solid sorbents. The filtration method uses for physically removal of air particles. According to Table S1, five methods for air filtration can be used [29, 30]. The air filtration have many disadvantages such as decreasing pressure, small loading of absorbent material and low surface area for removal of particles from air [31, 32]. In other hands, the solid sorbents (nano material) physically absorbed the

airborne particles from air with high surface area and removal efficiency more than filters and lower than chemically adsorption. Park et al. was reported that the carbon fiber ionizer (CFI) can be used for removal of aerosol from air. [33]. This method based on CFI is expensive and rigorous, while the present study is much easier and simpler and also has a high capacity than CFI. Another disadvantage of CFI was the ineffectiveness for depositing particles below 50 µm, but in proposed method, due to the presence of nanoparticles, particles below 50 µm can easily be absorbed without an escape from the adsorbent [34, 35]. Saylor et al. was reported a wet scrubbing method (WSM) for removing of aerosol particles from industrial sources [36]. These methods do well at removing a large fraction of the total aerosol from air, but usually perform poorly in removing nano and micro scale aerosols, which are particularly dangerous to humans. So, further research for improving of methods is needed [37, 38]. In setup of wet scrubbing technology for particle removal from air, water sprays are used to generate water drops which fall against the flow, collide with particles, eventually removing them in the process [39]. The drops generally used in wet scrubbers are on the

Table 4 Comparing of different sorbents for removal of lead oxide from air

Sample*	DAGS (Conc. ppb)	Added (Conc. ppb)	F-AAS ^a (Conc. ppb)	ET-AAS ^a (Conc. ppb)	FAAS Recovery(%)	ETAAS Recovery (%)
Blank	200	–	ND	5.3 ± 0.3	–	–
NH ₂ -UVM ₇	200	–	ND	35.6 ± 9.1	–	–
		100	ND	52.4 ± 6.8	–	16.8
HS-UVM ₇	200	–	193.5 ± 7.2	198.3 ± 9.1	–	–
		100	291.3 ± 8.4	302.5 ± 6.8	97.8	104.2
UVM ₇	200	–	ND	42.2 ± 9.1	–	–
		100	ND	64.8 ± 6.8	–	22.6
AC	200	–	ND	55.1 ± 9.1	–	–
		100	86.4	83.2 ± 6.8	–	28.1
COOH-UVM ₇	200	–	ND	32.3 ± 9.1	–	–
		100	ND	49.6 ± 6.8	–	17.3

^a Mean of three determinations ± confidence interval ($P = 0.95$, $n = 5$)

* (Air bag; 0.2 and 0.1 ppm in 1 Li bag, 0.1 mL min⁻¹ air flow rate, Peak Area, 10 mg, T = 25 °C, pH = 5)

order of 100 μm in diameter. An important downside to wet scrubbers, is that they perform poorly at removing particles less than one micron [40]. Recently, the different methods was used for removal VOCs, aerosols and dust from air [41–45]. The more information was discussed in text S17(ESM) by references.

Conclusion

In this study, nano sorbents such as; $\text{NH}_2\text{-UVM}_7$, HS-UVM_7 and UVM_7 was used for removal of pollutant lead aerosols from air by SLGPE method. The simple and applied method based on HS-UVM_7 was demonstrated for lead aerosols removal from air. The important factor included, lead aerosol concentration, mass of sorbent, temperature and air/ liquid flow rate were optimized. The capacity, recovery and efficiency of $\text{NH}_2\text{-UVM}_7$, HS-UVM_7 and UVM_7 was investigated and compared together. Based on results, the capacity and efficiency of HS-UVM_7 were more than $\text{NH}_2\text{-UVM}_7$ for lead nitrate aerosols from air. In addition, lead oxide aerosols (PbO) removed from air only by HS-UVM_7 by proposed method at optimized pH. The results showed, the air flow rate have more effected on removal of aerosols from air and caused to increase the recovery of extraction of air particles $\text{NH}_2\text{-UVM}_7$, HS-UVM_7 . Due to characteristics of sorbents, high surface area of HS-UVM_7 with chemically adsorption in liquid phase was lead to a high efficiency for lead removal from air (more than 95%) with high adsorption capacity as compared to physically adsorption in gas phase (less than 10% in air).

Supplementary information

The more information explained in Electronic Supplementary Material (ESM) which was included, Text: S1–S17, Fig. S1–S4 and Table S1.

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Compliance with ethical standards

Conflict of interest They have no conflict of interest in this work.

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