

MWCNT/nano-ZrO₂ as a new solid phase extractor: its synthesis, characterization, and application to atomic absorption spectrometric determination of lead

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Nanoscale ZrO₂ was synthesized on a multiwall carbon nanotube (MWCNT) and designed as a new solid phase extractor for metal ion preconcentration. The characterization of the synthesized material was achieved by transmission electron microscope (TEM) and X-ray diffraction (XRD). Then the new nanoscale material was applied to preconcentration of lead(II) from various matrices. Different experimental factors including pH of the sample solution, sample volume, flow rate of the sample solution, and volume and concentration of the eluent for the preconcentration step were examined. The effect of interfering ions on the recovery of the lead(II) was also investigated. The recovery of lead(II) under the optimum conditions was found to be 104 ± 2% at 95% confidence level. The preconcentration factor was 30 when 150 mL of sample solution and 5 mL of eluent were used. The analytical detection limit for Pb(II) was 0.80 µg L⁻¹ after preconcentration. The adsorption capacity of the new nanosorbent was 115 mg g⁻¹. The accuracy of the method was confirmed by analyzing standard reference materials (Silty Clay 7003). The results demonstrated good agreement with the certified values. The method was applied for the determination of lead in tap water and clay samples.

Key Words: Preconcentration, lead, nanosorbent, atomic absorption spectrometry, multiwalled carbon nanotube, zirconium dioxide

Introduction

Lead is a widely used heavy metal, especially in storage batteries, solders, cable sheaths, pigments, anti-knock products, household pumping systems, natural deposits, and radiation shields. It may be released into the

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environment from the above sources due to corrosion and erosion of lead-containing materials.¹ Inorganic lead may be absorbed through the gastrointestinal tract, the respiratory system, and the skin. Initially, lead is distributed in the blood, liver, and kidney; after prolonged exposure, as much as 95% of the body burden of lead is found in bone tissue. The main targets of lead toxicity are the hematopoietic system and the nervous system.² Provisional tolerable weekly intake (PTWI) of 25 $\mu\text{g kg}^{-1}$ of body weight was established for Pb by the FAO/WHO,³ which is equivalent to 214 $\mu\text{g day}^{-1}$ for an individual of 60 kg.⁴ Therefore, it is important to determine the trace lead from various samples. However, trace lead determination is still difficult due to insufficient sensitivity of the detection techniques, such as flame atomic absorption spectrometry, and possible matrix interferences.⁵ In order to overcome this problem, preliminary separation and/or preconcentration techniques are usually applied for the separation of trace metals from complex matrices into a known matrix.^{6–8} In recent years, among the separation and/or preconcentration techniques, solid phase extraction (SPE) has been extensively used due to its advantages such as operation simplicity, high preconcentration factor, reduced solvent usage, suitability to combine with different detection techniques, reduced disposal costs, shorter extraction times for sample preparation,^{9,10} and the availability of a wide variety of sorbent materials that mainly affect the extraction efficiency.

Different materials are used as sorbent such as resins,^{11,12} modified resins,^{13–15} silica,¹⁶ and nano-materials including carbon nanotubes^{17–22} for the SPE.^{23,24} Tajik and Taher developed a SPE method for separation and column preconcentration of Zn(II) on modified multiwall carbon nanotubes prior to its flame atomic absorption spectrometric determination. A preconcentration factor of 250 was achieved in this method.

In our literature survey, numerous papers were found on the separation and/or preconcentration of Pb(II) from various matrices. Soyak et al. developed a membrane filtration method for separation-preconcentration of Cu(II) and Pb(II) on acetate membrane as their 1-2-pyridylazo 2-naphthol (PAN) complexes.²⁵ He et al. used activated carbon functionalized by 2-((2-aminoethylamino)methyl)phenol for the preconcentration of Cu(II), Fe(III), and Pb(II).²⁶ Hazer et al. described an atomic absorption spectrometric determination of Cd(II), Mn(II), Ni(II), Pb(II), and Zn(II) ions in water, fertilizer, and tea samples after preconcentration on Amberlite XAD-1180 resin loaded with 1-(2-pyridylazo)-2-naphthol. They found the detection limit for Pb(II) to be 29 $\mu\text{g L}^{-1}$.²⁷ Mahmoud et al. studied the removal and preconcentration of Pb(II) and other heavy metals from water using physically adsorbed alumina on dithizone.²⁸ Burham et al. developed a new solid phase extractor by modifying Amberlite XAD-2 with 4'-(2-hydroxyphenylazo)-3'-methyl-1'-phenyl-2'-pyrazolin-5'-one. They reported the exchange capacity of the new material to be $5.35 \pm 0.04 \text{ mg g}^{-1}$ and the detection limit to be 2.8 $\mu\text{g L}^{-1}$ for Pb(II).²⁹ Zachariadis et al. developed a rapid and sensitive time-based flow injection method for on-line preconcentration and determination of Pb(II) by FAAS using polytetrafluoroethylene. They found the detection limit to be 0.8 $\mu\text{g L}^{-1}$ for Pb(II).³⁰ Baytak and Türker used Amberlite-572 and EDTA as solid phase extractor for the determination of lead and nickel by FAAS. They found the preconcentration factor of 50 and the detection limit of 3.65 ng mL^{-1} for Pb(II).³¹ In a different study, Baytak et al. developed a solid phase extractor by loading *Aspergillus niger* on silica gel for the determination of lead, iron, and nickel in water and vegetable samples. They found the recovery for Pb(II) to be $98 \pm 3\%$ and the detection limit to be 5.2 ng mL^{-1} .³² Hu and Ren studied the separation, preconcentration, and determination of Pb(II) in water samples using microcrystalline triphenylmethane loaded with quinolin-8-olate. They reported the preconcentration factor up to 200 and the detection limit 0.074 $\mu\text{g L}^{-1}$.³³ Suleiman et al. used bismuthiol-II-immobilized magnetic

nanoparticles to separate and preconcentrate Cr(III), Cu(II), and Pb(II). They found an enrichment factor of 87 and detection limit of 0.085 ng mL⁻¹ for Pb(II).³⁴ Kara developed a micelle-mediated extraction method for the preconcentration and determination of trace metals by flow injection and reported a detection limit of 17.9 ng mL⁻¹ for Pb(II).³⁵ Martinis et al. used tetradecyl(triethyl)phosphonium chloride ionic liquid single-drop microextraction for the determination of Pb(II) in water samples by ETAAS. They obtained a preconcentration factor of 32 and detection limit of 3.2 ng L⁻¹.³⁶

The objective of this research was to synthesize nano-ZrO₂ on MWCNT as a new solid phase extractor for metal ions enrichment. To the best of our knowledge, this is the first study to use this composite solid phase extractor for Pb(II) preconcentration. In this study, the synthesized material was first characterized by using various techniques such as TEM and XRD and then used as solid phase extractor for the separation and/or preconcentration of lead(II). The proposed procedure was validated by analyzing certified reference materials, and applied for the determination of lead(II) in real samples.

Experimental

Reagents and solutions

All reagents were of analytical grade, unless otherwise stated. A stock solution of lead (1000 mg L⁻¹, Merck, Germany) was used during the study. Working solutions of the lead ion were prepared by suitable dilution of the stock solution. A multiwall carbon nanotube (MWCNT) (MER Corporation, USA), Zr(OCl)₂.2H₂O (BDH), Ni(NO₃)₂.6H₂O (Carlo Erba, Italy), NaNO₃ (Carlo Erba, Italy), Ca(NO₃)₂.4H₂O (J.T. Baker, USA), KNO₃ (Merck, Germany), Cr(NO₃)₃.9H₂O (Carlo Erba, Italy), Co(NO₃)₂.6H₂O (Carlo Erba, Italy), Ni(NO₃)₂.6H₂O (Carlo Erba, Italy), Cd(NO₃)₂.4H₂O (Carlo Erba, Italy), HNO₃ (65%, Merck, Germany), HCl (37%, Merck, Germany), H₂SO₄ (98%, Merck, Germany), NH₃ (25%, Merck, Germany), HF (38%, Merck, Germany), and ultrapure water (18.3 MΩ.cm) were used. Ultrapure water was used to prepare all solutions.

Apparatus

The characterization of the synthesized material was performed by TEM and XRD methods. A Technai G2 120 kV transmission electron microscope (Oregon, USA) and a BRUKER D8 discover X-ray diffractometer (Madison, USA) were used for the determination of the morphology of the synthesized nanomaterial. The experimental conditions of XRD measurement were as follows: CuKα radiation; tube voltage/current, 20 kV/30 mA; scanning range (2θ), 5°-80°; scanning rate, 5°/min. A Varian (Palo Alto, CA, USA) AA240FS model flame atomic absorption spectrometer equipped with a deuterium-lamp background corrector, a lead hollow cathode lamp (Varian), and an air-acetylene flame as the atomizer was used for the determination of lead under the conditions suggested by the manufacturer. The wavelength, lamp current, slit width, and acetylene flow rate were 217.0 nm, 10 mA, 1.0 nm, and 13.5 L min⁻¹, respectively. All pH measurements were made with a WTW 720 model pH meter (Weilheim, Germany). A thermostat shaker (Nüve ST-402, Turkey), ultrasonic bath (Sonicator) (Bandelin electronic RK100H, Germany), and peristaltic pump (Watson Marlow 323, USA) were used for the adsorption experiments.

Preparation of material

Nano-MWCNT/ZrO₂ was synthesized by the procedure given in the literature³⁷ for synthesizing ZrO₂ in the presence of MWCNT. As the first step, MWCNT was treated with a concentrated acid mixture to remove catalyst residuals from MWCNT for purification and to increase the surface area and specific pore volume of MWCNT.^{38,39} For this purpose, MWCNT was refluxed in a concentrated H₂SO₄-HNO₃ (1:2 v/v) mixture at 100 °C for 24 h. Next, MWCNT was filtered and washed with water to remove acid residuals. Then 1.25 g of acid-treated MWCNT and 3.0 g of Zr(OCl)₂ were put in 50 mL of water-ethanol (5:3 v/v) mixture. After that, 1.5 mL of Triton X-114 was added to the mixture as surfactant. The mixture was stirred for 90 min, and then sonicated for 30 min in an ultrasonic bath. Then Zr(OH)₂ was precipitated from the mixture by adjusting the pH to 5-6 with NH₃. After sonication again for 15 min, the mixture was dried at 65 °C for 2 h. The obtained solid material was taken in a porcelain crucible and heated at 850 °C in a furnace under argon atmosphere for 2 h, and a white powder was obtained.

Column preparation

A glass column (150 mm length, 8 mm i.d.) with glass wool over its stopcock was used. A total of 200 mg of synthesized nanocomposite material (MWCNT/nano-ZrO₂) was made slurry in water and then placed into the column. A small amount of glass wool was placed on top to avoid disturbance to the adsorbent during sample passage. The column was preconditioned by passing a blank solution having the same pH with the sample solution prior to use. After each use, the nanomaterial in the column was washed with dilute HCl (1 mol L⁻¹) and with water consecutively and stored in water for the next experiment.

Preconcentration and determination procedure

The proposed preconcentration procedure was tested with model solutions prior to the determination of trace lead in real samples. An aliquot of a solution (25 mL) containing 0.4 µg of the lead(II) was placed in a beaker and the pH of the solution was adjusted to 4 by using diluted HCl or NH₃ solution. The column was preconditioned by passing the solution of pH 4 through the column and then the model solution was passed through the column at a flow rate of 2 mL min⁻¹. The adsorbed lead(II) ions on the column were eluted by using 5 mL of 1 mol L⁻¹ hydrochloric acid solution. The eluent was analyzed for the determination of lead concentration by FAAS. The column was used repeatedly after washing with 10 mL of 1 mol L⁻¹ hydrochloric acid solution and ultrapure water consecutively. Using the procedure described above, the recovery of the lead was calculated from the ratio of the concentration found by FAAS and the concentration calculated theoretically.

Preparation of samples

A tap water sample was collected from the city of Ankara, Turkey, and filtered through blue ribbon filter paper before use. A clay sample was collected from Mihallıccık, Eskişehir, another city in Turkey. Approximately 0.25 g of clay sample and 0.25 g of standard reference clay (Silty Clay 7003) were placed in PTFE beakers. For dissolution, 4 mL of concentrated nitric acid was added. The beaker was heated on a hot plate at 130 ± 10 °C for 1 h. After cooling to room temperature, 1 mL of hydrofluoric acid was added dropwise. The beaker was

heated until complete decomposition of the sample and then left for sample evaporation nearly to 2 mL. The resulting solution was transferred into a 50-mL volumetric flask by washing the interior surface of the beakers with HNO₃ (0.5% v/v) 3 times and diluted to the mark with ultrapure water. A blank solution was prepared by using the procedure given above.

Results and discussion

Characterization of synthesized material

The synthesized nanoscale MWCNT/ZrO₂ composite material was characterized by transmission electron microscope (TEM) and X-ray diffraction (XRD). Figures 1 and 2 show TEM images of nanoscale MWCNT/ZrO₂. The abundant presence of nanoscale MWCNT/ZrO₂ is clearly shown. A TEM image reveals that the MWCNT/ZrO₂ particles are very fine and the grain size is about 35-75 nm. In order to characterize the nature of the synthesized material, the XRD pattern of the material was also investigated. First of all, a XRD pattern of acid-treated MWCNT was obtained and is shown in Figure 3 in order to ensure that the final material consists of MWCNT together with ZrO₂. As shown in Figure 4, the synthesized material exhibits diffraction peaks centered at about 24.6°, 28.4°, and 31.5°. These peaks are characteristic of the zirconium oxide and suggest that the sample is present mainly in the monoclinic phase (ICDD pattern catalog number 03-065-1024).⁴⁰ This result is in accordance with the data reported by Cordova-Martinez et al. for nanocrystalline zirconia.⁴¹ Other peaks shown in the XRD pattern indicate the coexistence of a tetragonal phase.^{41,42} The diffraction

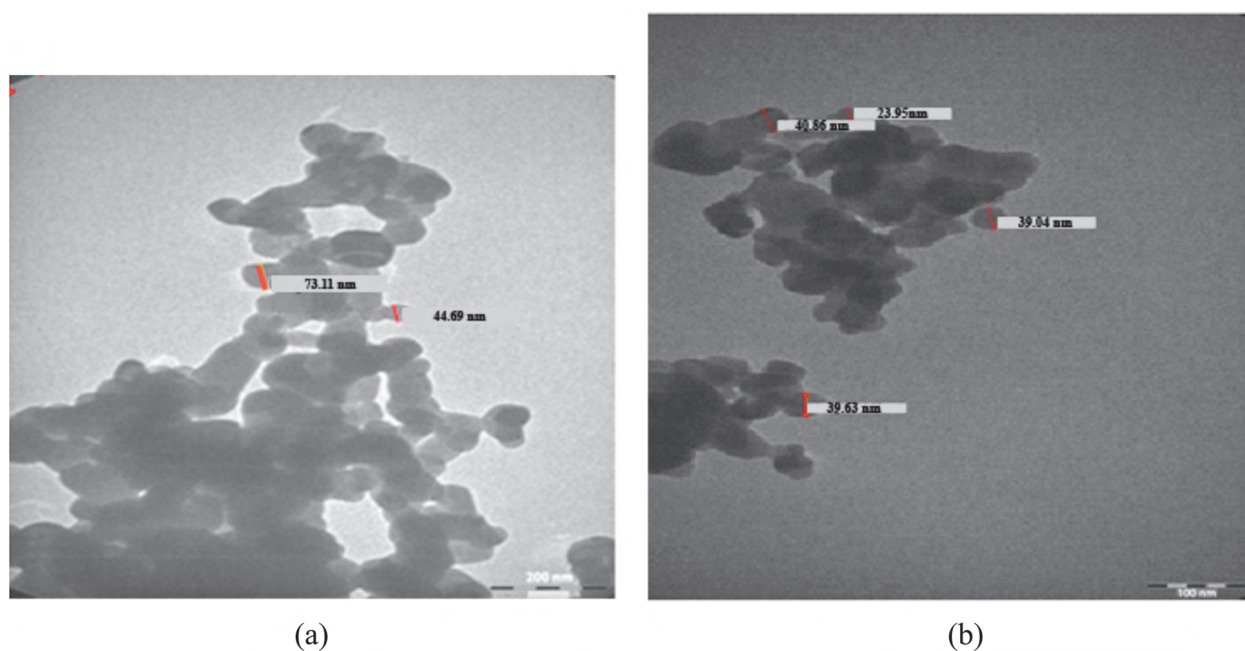


Figure 1. a) TEM micrograph of synthesized material. b) TEM micrograph of synthesized material from a different angle.

peaks obtained match well with data given for zirconium oxide nanocrystals in the form of monoclinic and tetragonal phases.^{41,42} Treating the samples at higher temperature such as 1000 °C dominates the formation of the monoclinic structure. Previous studies show that the monoclinic phase is more stable as the annealing temperature increases.⁴² These results also show that the synthesized material (treated at 850 °C) is mainly monoclinic zirconia. As a result, it can be concluded that the synthesized new nanomaterial consisted mainly of ZrO₂ and MWCNT.

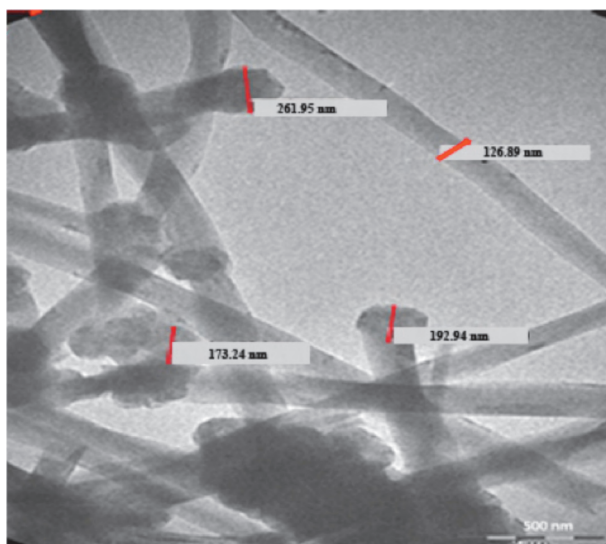


Figure 2. TEM micrograph of MWCNT.

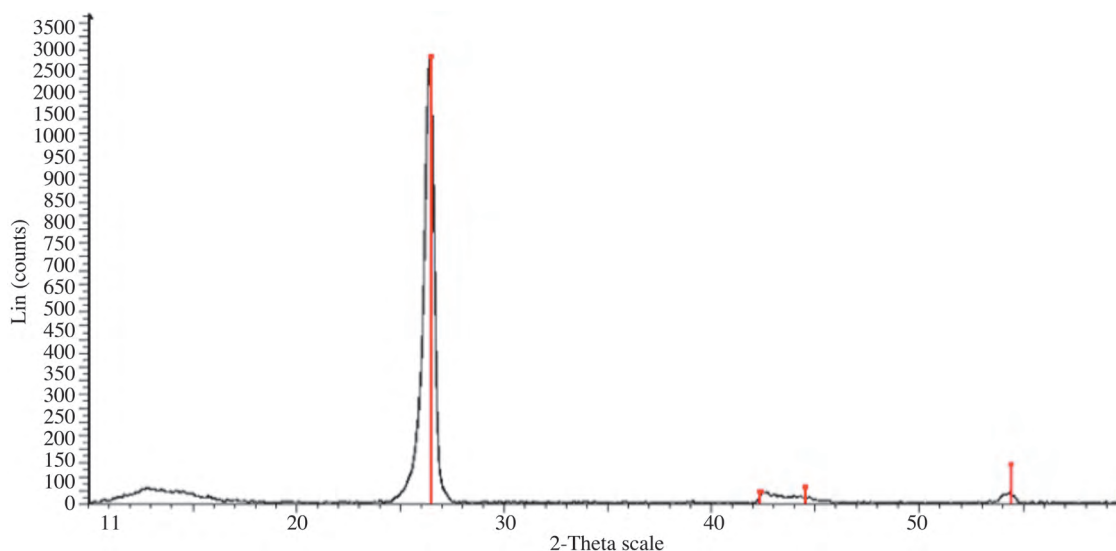


Figure 3. XRD graph of acid-treated MWCNT.

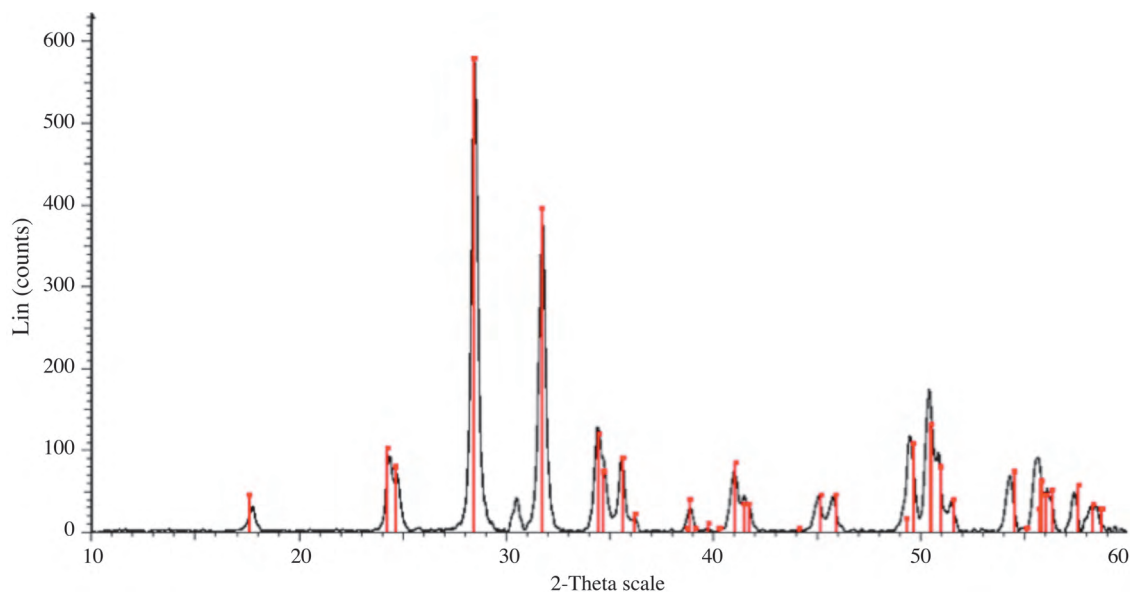


Figure 4. XRD graph of MWCNT/nano-ZrO₂ composite.

Effect of pH on the recovery of Pb

The pH value plays an important role in the adsorption of ions on sorbents. pH also strongly influences the speciation and the sorption availability of the heavy metals. Therefore, the retention of metal ions on the column containing nanomaterial synthesized was studied as a function of pH. For that purpose, the pH values of synthetic sample solutions prepared as given in the “Preconcentration and determination” section were adjusted to a range of 2-10 with HCl or NH₃ solutions keeping the other parameters constant and the general preconcentration procedure was applied. As shown in Figure 5, the optimum pH of the sample solution was 4 for Pb(II). At this pH value, the recovery of the Pb(II) is above 95% (N = 7). The decrease in the recovery of Pb(II) at the lower pH values could be due to the competition between protons and the Pb(II) for the adsorption sites of the sorbent. Therefore, a pH of 4 was selected in further experiments.

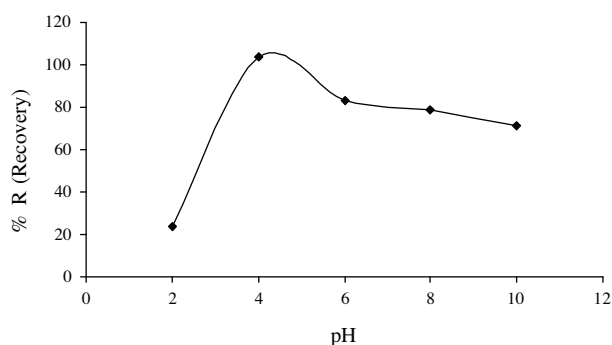


Figure 5. Effect of pH on the recovery of Pb(II) following its sorption on MWCNT/nano-ZrO₂ composite.

Effect of eluent concentration on the recovery of Pb

The type and concentration of eluent is also important for the analytical performance of a column solid phase preconcentration system. Because the adsorption of lead(II) is negligible at pH < 4, 5 mL of 0.5 mol L⁻¹ and 1 mol L⁻¹ HCl and HNO₃ were tested for desorption of retained Pb(II) from the nanosorbent. As a mean of 3 replicates plus standard deviation, the recoveries of 100 ± 2, 100 ± 4, 100 ± 3, and 100 ± 3 were obtained for 0.5 mol L⁻¹ HCl, 1.0 mol L⁻¹ HCl, 0.5 mol L⁻¹ HNO₃, and 1.0 mol L⁻¹ HNO₃, respectively. As a result of the experiments, all of the tested eluents were found to be satisfactory for Pb(II) (recovery > 95%). However, we chose 5 mL of 1.0 mol L⁻¹ HCl solution for further experiments.

Effect of flow rate of sample solution on the recovery of Pb

The retention of element on an adsorbent depends upon the flow rate of sample solution. Therefore, it was examined under optimum conditions (pH, eluent type, etc.) by applying the general procedure. The synthetic lead solution (25 mL, containing 0.4 µg of Pb(II)) was passed through the column with the flow rates adjusted in a range of 2-12 mL min⁻¹ by a peristaltic pump. The optimum flow rate was found to be 12 mL min⁻¹ and so was selected for further experiments. The flow rate of elution solution was 12 mL min⁻¹.

Effect of sample volume on the recovery of Pb

In order to determine the maximum applicable volume of sample solution (or minimum applicable concentration of the analytes), the effect of the volume of sample solution passed through the column on the retention of analytes was investigated. For that purpose, 50, 100, 150, 200, 250, and 500 mL of sample solutions containing a fixed amount of lead(II) corresponding to 0.2, 0.1, 0.067, 0.05, 0.04, and 0.02 µg mL⁻¹ of Pb(II), respectively, were passed through the column under the optimum conditions determined experimentally. It was found that Pb(II), up to 150 mL of sample solution, could be recovered quantitatively. At higher sample volumes, the recoveries decreased gradually with increasing volume of sample solution. Because the elution volume was 5 mL, a preconcentration factor of 30 was obtained for Pb(II). It can be concluded that 0.067 µg mL⁻¹ Pb(II) could be determined by this method for 150 mL of sample volume. However, Pb(II) cannot be determined directly by FAAS with sufficient accuracy at these low concentrations.

Column reusability

The stability and potential reusability of the adsorbent were assessed by monitoring the change in the recoveries of analytes through several adsorption-elution cycles. The regeneration ability and stability of the column were investigated by passing the analyte solution and then passing 10 mL of 1 mol L⁻¹ HCl and 50 mL of ultrapure water through the column packed with 200 mg of MWCNT/ZrO₂ nanocomposite. The adsorbent was always stored in water when it was not in use. It was observed that the column could be reused for up to 100 runs without a decrease in the recoveries of the lead(II).

Adsorption isotherms and adsorption capacity of nano-MWCNT/ZrO₂

The adsorption capacity is an important factor in the evaluation of the property of a sorbent, because it determines how much sorbent is required to quantitatively concentrate the Pb(II) from a given solution. To determine the adsorption capacity, 50-mL sample solutions containing 20, 50, 100, 200, 300, 400, and 500 $\mu\text{g mL}^{-1}$ Pb(II) were adjusted to pH 4 and a batch procedure was applied by using 100 mg of MWCNT/ZrO₂ nanomaterial. The solutions were shaken for 2 h at 120 rpm at room temperature. After shaking, 10 mL of supernatant was taken from each solution and the amount of residual Pb(II) in the solution was determined by flame atomic absorption spectrometry.

The data of the isotherm reveal that the adsorption process conforms to the Langmuir model. In Figure 6, the graph shows an excellent fit to the data in the concentration interval studied in all cases for the Langmuir model. A modified Langmuir equation conformed to this kind of adsorption isotherm as represented below:

$$\frac{C_E}{Q_E} = \frac{C_E}{Q_0} + \frac{1}{Q_0 b}$$

where C_E is the concentration of Pb(II) in the solution at equilibrium (mg L^{-1}), Q_E is the amount of sorbed Pb(II) per gram of sorbent at equilibrium (mg g^{-1}), b is the “affinity” parameter or Langmuir constant (L mg^{-1}), and Q_0 is the “capacity” parameter (mg g^{-1}). Based on the linearized form of the adsorption isotherm derived from plots of C_E/Q_E vs. C_E , the constants Q_0 and b values were calculated from the slope and intercept of the graph (Figure 6). Langmuir adsorption capacity (Q_0) and Langmuir constant (b) were found to be 115 mg g^{-1} and 0.003 L mg^{-1} , respectively.

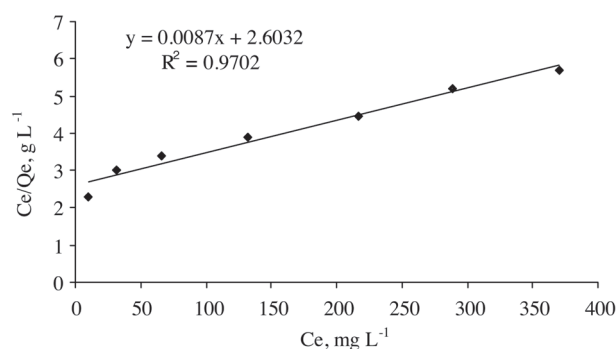


Figure 6. Linearized Langmuir isotherm obtained from the Pb(II) adsorption on MWCNT/nano-ZrO₂ composite.

Effect of interfering ions

Interferences from alkali metal ions [Na and K], alkaline earth metal ions [Ca], which are found generally in high concentration in water samples, and Cd, Cr, Ni, and Co as their nitrate salts on the preconcentration of the studied analyte were investigated (Table 1). In these experiments, solutions of $0.016 \mu\text{g mL}^{-1}$ of Pb²⁺ containing the added interfering ions were treated according to the recommended procedure. There was no obvious influence on the adsorption of Pb(II) for Ca and Co up to $5000 \mu\text{g mL}^{-1}$; for Cd(II), Cr(III), Ni(II), and K up to $500 \mu\text{g mL}^{-1}$; and for Na ions up to $50 \mu\text{g mL}^{-1}$. As can be seen, the possible matrix ions studied had no considerable effect on the determination of Pb(II). However, the tolerance limit for Na ions

is unexpectedly quite low. It can be seen from the literature that alkaline metals are not usually sorbed by the sorbents widely used and so higher tolerance limits are obtained. In this study, a relatively low tolerance limit was obtained for Na ions compared to the results given in the literature. This feature may prevent the determination of lead in salty samples containing above 50 $\mu\text{g mL}^{-1}$ Na ions.

Table 1. The effect of some foreign ions on the recovery of Pb(II).

Interfering ions	Concentration (mg L ⁻¹)	Recovery ^a (%)
Na ⁺	-	104 ± 2
	5	102 ± 2
	50	104 ± 2
	250	89 ± 3
K ⁺	-	104 ± 2
	5	103 ± 2
	50	104 ± 2
	500	103 ± 3
Ca ²⁺	5	104 ± 2
	50	104 ± 2
	500	103 ± 2
	2500	104 ± 3
	5000	104 ± 3
Cd ²⁺	5	102 ± 2
	50	102 ± 3
	500	102 ± 4
	750	87 ± 2
Cr ³⁺	5	101 ± 2
	50	100 ± 2
	500	102 ± 3
	750	89 ± 3
Ni ²⁺	5	103 ± 3
	50	103 ± 3
	500	102 ± 2
	750	89 ± 2
Co ²⁺	5	100 ± 2
	50	104 ± 3
	500	103 ± 3
	5000	103 ± 2

^aMean ± standard deviation for the 3 determinations.

Analytical features

By using direct aspiration in FAAS without applying the preconcentration system the linear range for lead determination was between 80 and 5000 $\mu\text{g L}^{-1}$.

In order to determine the instrumental detection limit, 50 mL of blank solution was adjusted to pH 4 and then this solution was passed through the column. Blank solution was prepared by adding a minimum amount of lead to the ultrapure water in order to obtain a readable lead signal. The column was washed with 50 mL of 1 mol L⁻¹ hydrochloric acid solution (with no preconcentration). The instrumental detection limit based on the mean of blank values plus 3 times the standard deviation of the blank values was found to be 24 $\mu\text{g L}^{-1}$ for lead (N = 20). The analytical detection limit calculated by dividing the instrumental detection limit by the preconcentration factor (30) was 0.8 $\mu\text{g L}^{-1}$.^{43,44}

In order to determine the precision of the method, it was applied successively by using 25 mL of model solutions containing 0.4 $\mu\text{g mL}^{-1}$ Pb(II) under the optimum conditions. The Pb(II) in elution solution was determined by FAAS. The mean recoveries for 7 determinations at 95% confidence level were $104 \pm 2\%$ for Pb(II). The percent relative standard deviation of recoveries was $\leq 2.0\%$.

In order to evaluate the accuracy of the developed procedure, lead was determined in the standard reference material (Silty Clay 7003). Lead concentration found as the mean of 5 determinations at 95% confidence level was $32 \pm 3 \mu\text{g g}^{-1}$ with a relative error of 4.5%. It was found that there was no significant difference between the result found by the proposed method and the certified value ($33.5 \pm 2.4 \mu\text{g g}^{-1}$) according to Student's t-test ($t_{\text{calculated}} = 1.39$ and $t_{\text{critical}} = 2.78$, N = 5). It can be concluded that there is no systematic error in the determination at 95% confidence level.

Application

In order to show the applicability of the method, it was applied for the determination of lead in tap water and clay samples under optimal experimental conditions. The accuracy of the method was also checked by measuring the recovery of spiked real samples. The results obtained are given in Table 2. Relative errors, below 5%, demonstrate the applicability and independence from matrix constituents of the samples. The proposed technique can be successfully applied to environmental samples for the determination of traces of Pb(II). Some comparative data about lead preconcentration by other sorbents are summarized in Table 3.

Table 2. Determination of lead(II) in various samples (volume of tap water sample: 100 mL, amount of clay: 0.25 g).

Sample	Added	Found ^a $\bar{x} \pm \frac{ts}{\sqrt{N}}$	Error %
Mihallıccık clay	-	$0.3 \pm 0.2 \mu\text{g g}^{-1}$	-
	$5 \mu\text{g g}^{-1}$	$5.2 \pm 0.5 \mu\text{g g}^{-1}$	-1.9
Tap water	-	$0.35 \pm 0.06 \mu\text{g mL}^{-1}$	-
	$1 \mu\text{g mL}^{-1}$	$1.30 \pm 0.01 \mu\text{g mL}^{-1}$	-3.7

^aMean of 5 determinations at 95% confidence level.

Table 3. Comparative data on various sorbents for Pb(II) preconcentration.

Sample	Adsorbent and preconcentration technique	Determination technique	PF*	LOD* μg L ⁻¹	Reusability	Refs.
Water, Herbal	Sodium dodecyle sulfate-1-(2-pyridylazo)-2-naphthol modified nanometer-sized alumina, column SPE technique	FAAS	250	0.17	-	20
Food, water, geologic	Acetate membrane	FAAS	20	3.5	-	25
Water, biologic	2-((2-aminoethylamino)methyl) phenol functionalized activated carbon, column SPE technique	ICP-OES	100	0.16	10	26
Water, vegetable	Ambersorb-572 with EDTA, column SPE technique	FAAS	75	3.65	-	31
Water	Bismuthiol-II-immobilized magnetic nanoparticles, sonicated batch SPE technique	ICP-OES	87	0.085	-	34
Tap water, clay	MWCNT- nanoscale zirconium dioxide composite, column SPE technique	FAAS	30	0.8	100	This work

*Data given only for Pb(II).

FAAS: Flame atomic absorption spectrometry; ICP-OES: Inductively coupled plasma optical emission spectrometry; LOD: Limit of detection; PF: Preconcentration factor.

Conclusion

MWCNT/nano-ZrO₂ composite material as a new solid phase extractor provides a simple, selective, accurate, economical, rapid, and precise method for the preconcentration and determination of lead. There is no need for loading of any chelating and/or complexing agent or microorganism onto the sorbent or for using chelating and/or complexing agent before the preconcentration procedure to obtain quantitative recovery of lead ion. This minimizes possible contamination and interferences due to low reagent consumption. This feature also allows high repeated use of sorbent because there is no immobilized complexing or chelating agent that may be lost with repeated use. It was also found that the recovery values of the Pb(II) after 100 cycles of adsorption and desorption were still quantitative. Another advantage of the method is its permitting to study in acidic medium, minimizing precipitation of metal hydroxides. The enrichment factor, detection limit, and adsorption capacity of this new nanosorbent for lead are also satisfactory. The detection limit can be improved by using more sensitive detectors such as ICP-AES and ICP-MS. The results acquired from the analyses of the standard reference material confirmed the reliability of the method. The proposed technique can be successfully applied to environmental samples for the determination of traces of Pb(II).

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