Journal of Materials and Electronic Devices 3 (2023) 13-18

FYTRONIX JOURNAL OF MATERIALS AND ELECTRONIC DEVICES JMED http://dergi-fytronix.com/

Utilizing NiO Nanoflowers for Lead Measurement in Real Samples

Elif Aybike Berberoğlu[1], Elvan Hasanoğlu Özkan[2], Nurdan Kurnaz Yetim[1], Cemile Özcan[1*]

[1]Kırklareli University, Faculty of Arts and Sciences, Department of Chemistry, Kırklareli, Turkey
[2]Gazi University, Faculty of Sciences, Department of Chemistry, Ankara, Turkey

In this study, lead (Pb^{2+}) ions were determined by flame atomic absorption spectrophotometry (FAAS) using solid phase extraction (SPE) method by NiO nanoflowers and their absorption amounts were determined. Nickel oxide (NiO) nanoflowers were prepared by hydrothermal method and characterized using spectroscopic and microscopic methods. Analytical recovery efficiencies for Pb^{2+} were investigated by optimizing parameters such as eluent type, pH, sample volume and time from adsorption conditions for nanoflowers. Reproducibility results showed that elemental recovery was higher than 99%. Standard reference material analysis was performed to prove the accuracy of the solid phase extraction method with nanoflower for trace level Pb^{2+} metal analysis. Relative standard deviation values were found to be less than 10%.

Keywords: *NiO, Nanoflower, SPE, Heavy metal, Lead*

Submission Date: 29 June 2023
Acceptance Date: 15 August 2023

**Corresponding author: cemilebal.ozcan@klu.edu.tr*

1. Introduction

Nanoparticles are defined as materials in the size range of 1.0-100.0 nm. Due to the very small size of nanoparticles, the ratio of surface area to mass is very large and this characteristic increases the reactivity and applicability of nanoparticles [1-3].
Nanoparticles are classified according to their physicochemical properties, size, and morphological shape [4]. The main classes of nanoparticles are polymeric nanoparticles, semiconductor nanoparticles, ceramic nanoparticles, metallic nanoparticles, carbon-based nanoparticles, and lipid-based nanoparticles, while nanocrystals, nanorods, nanowires, nanowires, nanotubes and nanoflowers are classified according to their shape. [5]
Nanoflower structures, a subclass of nanoparticles, are relatively new nanomaterials that have attracted the attention of scientists for different applications.

Like other nanomaterials, the surface morphology of nanoflowers cannot be seen with the naked eye, but when examined microscopically, they appear as formations resembling flowers, and in some cases bouquets or trees. Thanks to the layered petals of nanoflower structures, which can be obtained by simple synthesis methods, their adsorption capacity, electrocatalytic activity, loading capacity and stability are quite high. For this reason, nanoflowers are finding application in health and environmental studies such as catalysis [6], bio/gas sensors [7], biomedical imaging [8,9], biocidal applications [10], wastewater treatment [6].
Today, the rapid increase in the world population, the diversification of human needs, developing technology and increasing industrialization bring environmental problems all over the world. In the industrial processes followed in the industry, large amounts of clean water are used for various purposes and because of the completed process, large amounts of wastewater are released into the environment. Depending on the source, wastewater released into the environment contains different organic/inorganic pollutants that are toxic and difficult to break down, persist in the environment for a long time, and therefore, can pose significant threats to living health/organisms [11,12].

Monitoring these pollutants in wastewater released into the environment and implementing effective remediation techniques becomes inevitable for organisms to thrive in their natural environment. In recent studies, researchers have been using nanomaterials with high selectivity and sensitivity to these pollutants. It is clearly seen in the literature that the preferred nanostructured materials allow easy removal of pollutants in the environment and are also used in the quantification of trace elements [13-15].

Flame atomic absorption spectrophotometry (FAAS) is widely used as a simple, low-cost, and efficient tool for the determination of many elements and allows the direct analysis of liquids [16]. However, for several reasons, such as matrix effects, low nebulization efficiency and low sensitivity, trace determination of elements using FAAS is not always possible. An alternative approach to purchasing expensive instruments to overcome the low sensitivity of FAAS is to use microextraction methods, which can separate the analytes of interest from the sample matrix and concentrate them to quantities that can be easily detected and quantified [17].
The past two decades have seen significant breakthroughs in the development of different micro extraction methods for both organic and inorganic compounds. In general, sample preparation involves (i) pre-concentration and enrichment of the target analyte(s), (ii) isolation and separation from the sample matrix, and (iii) obtaining a more compatible and detectable species. The applications of conventional sample preparation methods such as SPE and liquid-liquid extraction (LLE) have been limited due to some drawbacks such as large consumption of hazardous organic solvents, solvent losses, and labor-intensive process. To overcome these disadvantages, dispersive solid phase extraction (DSPE) has been developed, based on concepts like SPE, where sorbent particles are dispersed throughout the sample solution. This pre-enrichment method is widely used for the extraction and determination of a wide range of target analytes, despite its limitations, including the possibility of sorbent degradation and the difficulty of sorbent deposition. The adsorption capacity of adsorbents can be improved by using nanomaterials with superior surface area [16-18].

In the present study, NiO in nanoflower structure was synthesized by hydrothermal method in the presence of environmentally friendly solvents following the experimental procedure of Kurnaz Yetim et. al. [19] and used as adsorbent for the removal of heavy metal Pb^{2+} from real sample media (*Such as*: Wastewater and spinach leaves).

The experimental results show that the synthesized NiO nanoflower can be a good candidate for environmentally friendly adsorbent that can allow the extraction of many other pollutants / lead and other heavy metal ions from aqueous systems with high performance.

2. Experimental

2.1. Mateials

The X-ray diffraction analysis used a RIGAKU miniflex600 X-ray diffractometer with a Ni-filtered Cu Kα source. The scanning range was $10° < 2\theta < 90°$. Additionally, the surface morphology of the nanoflowers was examined using scanning electron microscopy (SEM). A FEI Quanta 400F with an EDX apparatus was used for the EDX analysis. For liquid extraction, ISOLAB brandsound wave-supported ultrasonic was employed. The Quantachrome Corporation's Autosorb-6 was used to characterize the pore size. Agilent hollow cathode lamps were employed to identify the analytes (Pb) in the analytical process utilizing the Agilent 240 AA Duo type Atomic Absorption Spectrometer.

2.2. Hydrothermal synthesis of NiO nanoflower

0.5 g $NiCl_2.6H_2O$ and 0.250 g urea $[CO(NH_2)_2]$, were dissolved in deionized water-ethanol (10:30 mL) with a magnetic stirrer for 30 min. The resulting solution was placed in a Teflon-lined steel autoclave and kept in an oven at 150 ºC for 12 *h*. After cooling to room temperature, the precipitate was centrifuged. The solid phase was washed several times with deionized water and ethanol and dried in an oven at 80 ºC for 24 *h*. The dried NiO nanoflower was calcined in a muffle furnace at 400 ºC for 1 *h*, increasing by 2 ºC/min from 150 ºC to 400 ºC. [19].

2.3. Solid phase extraction procedure

50 mg NiO, 10 mL deionized water, 0.25 mL (50 ppm) Pb^{2+} metal ion solution and 1 mL pH:6 buffer were added into 50 mL test tubes. The pH of the solution was adjusted to 6. The total volume was made up to 25 mL with ultrapure water. The samples were then kept in an ultrasonic bath for 10 minutes and centrifuged at 9000 rpm for 10 min. The liquid phase was saved for analysis and 5 mL of the selected acid solution was added to the solid phase. The samples were first kept in an ultrasonic bath for 10 min and then centrifuged at 9000 rpm for 10 min. The concentration of metal ions remaining in the liquid phase was analyzed by FAAS [14,15].

In the eluent type optimization step, 0.1-3.0 M HNO_3 and 1 M HCl acid solutions were used. At the pH optimization, pH values of 5-8 were used. In adsorbent amount optimization, 50-200 mg NiO nanoflower was used. In eluent volume optimization, 5-30 mL of ultrapure water was used. Finally, the optimum time was studied by keeping the samples in an ultrasonic bath for 5-60 min.

3. Results

3.1. Characterization of NiO nanoflowers

For the characterization of the structures of NiO nanoflowers prepared by hydrothermal method; FT-IR, XRD, FESEM, EDX analyses were performed. Figure 1 shows the FT-IR spectrum of NiO nanoflowers in the frequency range of 4000-400 cm^{-1}. When the FT-IR spectrum of NiO nanoflower is examined, the absorption band in the 490-430 cm^{-1} region belongs to υ(Ni-O), the broad band in the 3500-3300 cm^{-1} region belongs to υ(O-H) stretching vibration.

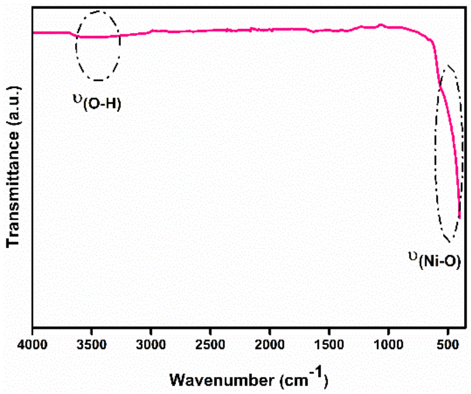

Fig. 1. FT-IR spectrum of NiO nanoflower

The crystal phase of NiO nanoflower is shown in Figure 2. The diffraction peaks of the NiO nanoflower structure were observed at 37.14°, 43.18°, 62.72°, 75.38°, 79.3°. From the XRD pattern, the five main peaks of the NiO sample corresponding to the crystallographic planes of (1 1 1), (2 0 0), (2 2 0), (2 2 0), (3 1 1), (2 2 2) can be well indexed to the NiO standard spectrum. In addition, the XRD pattern does not show any impurity peaks. These results indicate that the crystallinity of NiO nanoflower is high.

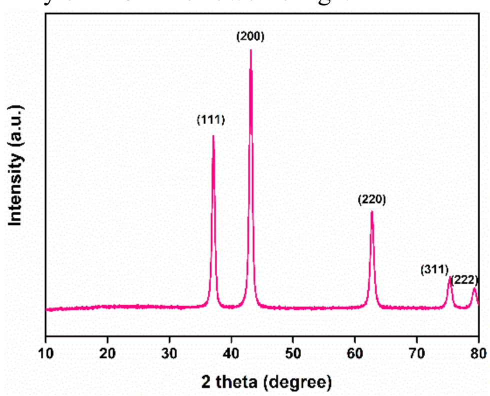

Fig. 2. XRD patterns of NiO nanoflower

The FESEM image of the NiO nanoflower structure is shown in Figure 3. It can be seen from the images that the nanofluids are composed of nanofibers. The thickness of the nanofibers was found to be less than 50 nm and the length of the fibers was less than 800 nanometers. The fibers are randomly aggregated as the nanofluids are composed of accumulated nanofibers from which ball-like structures are formed. Since the nanofibers accumulate randomly without any direction, the porosity of the nanofluids was found to increase where gaps between the fibers could be detected.

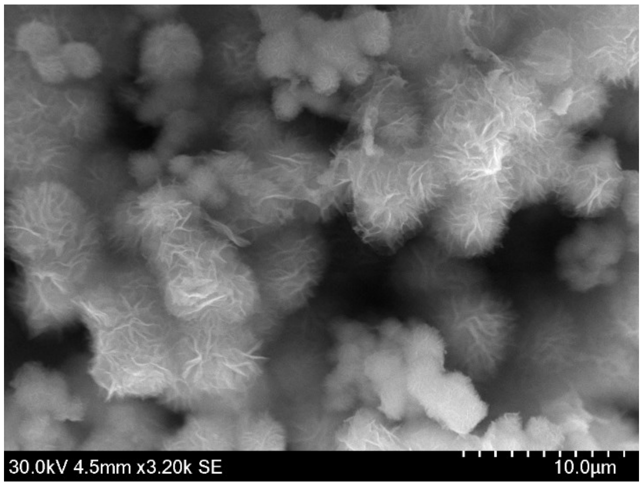

Fig. 3. FESEM image of NiO nanoflowers

Figure 4 shows the EDX spectrum results of the NiO nanoflower structure. Pure Ni and O peaks are identified in this spectrum.

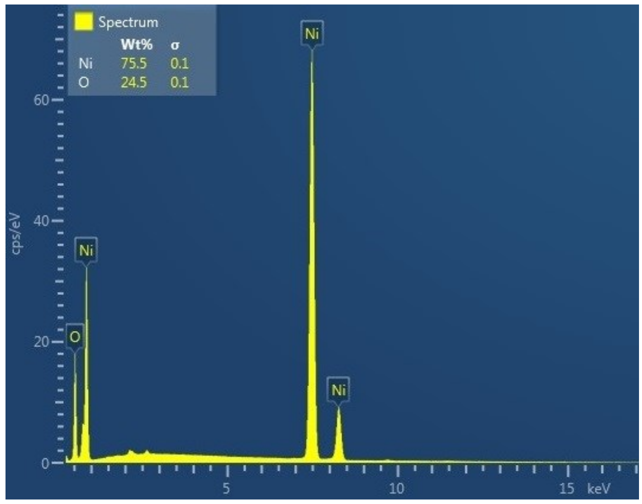

Fig. 4. EDX spectrum of NiO nanoflower structure

3.2. Removal of heavy metals (Pb^{2+})

3.2.1. Effect of eluent type

Different concentrations of HNO_3 (0.1-3.0 mol L^{-1}) and 1 M HCl acid solution were used for the elution of trace Pb^{2+} adsorbed on NiO nanoflowers. The results are given in

Figure 5. In the graph, the best recovery of Pb^{2+} metal ion was found to be in 1 M HNO_3 with 87.2% efficiency.

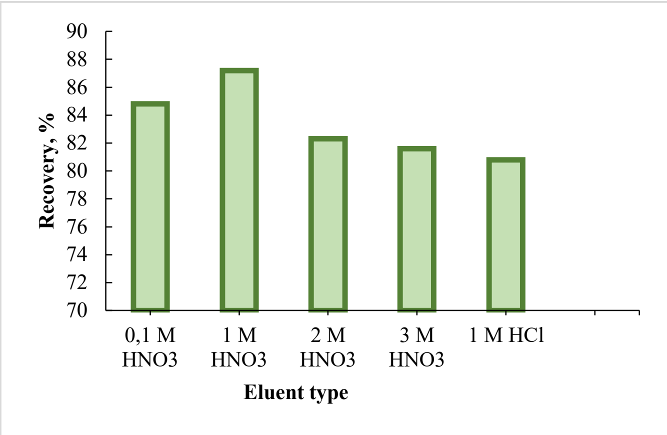

Fig. 5. Eluent type screening of Pb^{2+} for NiO nanoflower

3.2.2. Effect of pH

The recovery effect of the pH of the model solution for Pb(II) metal ion on NiO nanoflowers was investigated in the pH range 5.0-8.0. The results are presented in Figure 6. When the graph is analyzed; it was determined that the best recovery of Pb^{2+} metal ion was at pH 6.5 with 97.2% efficiency.

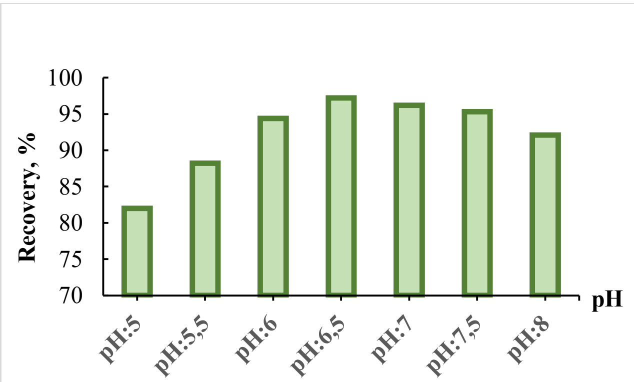

Fig. 6. pH screening of Pb^{2+} ion for NiO nanoflower

3.2.3. Effect of adsorbent amount

The effects of the amount of NiO nanoflowers on the separation-enrichment performances of Pb^{2+} metal ion in the range of 50-150 mg were investigated. Figure 7 shows that the best recovery of Pb^{2+} metal ion was determined at 50 mg adsorbent with 98% efficiency.

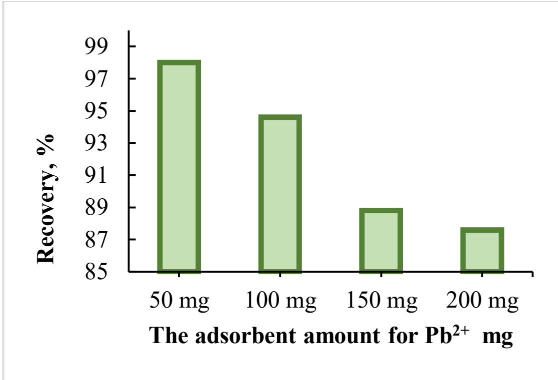

Fig. 7. Quantification screening for NiO nanoflower for Pb^{2+} recovery

3.2.4. Effect of sample volume

Sample volume is a critical parameter to achieve a high enrichment factor in extraction studies [20]. To achieve a high enrichment factor, the effect of sample volume on Pb^{2+} recoveries on nio nanoflowers was studied in the range of 5-30 mL sample volume. Figure 8 shows that the best recovery was found to be at 20 mL with 98.9% efficiency.

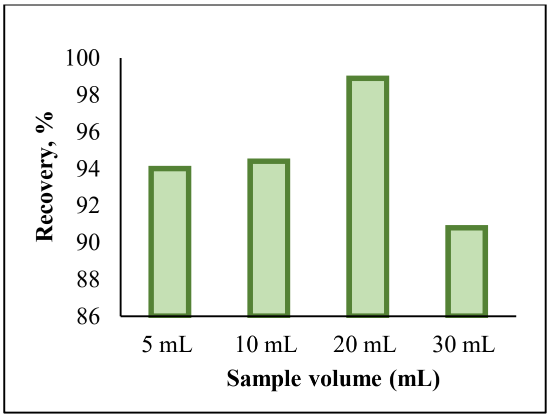

Fig. 8. Solution volume screening for NiO nanoflower for Pb^{2+} recovery

3.2.5. Effect of sonication time

To trigger the adsorption of analyte ions, the solutions were sonicated in an ultrasonic bath. Different sonication times between 5 min and 60 min were used to evaluate the effect of sonication on Pb^{2+} recovery. The graph showing the effect of sonication time on the recovery efficiency of Pb^{2+} is presented in Figure 9. The optimum recovery sonication times for Pb^{2+} were found to be 30 min and 99.2%.

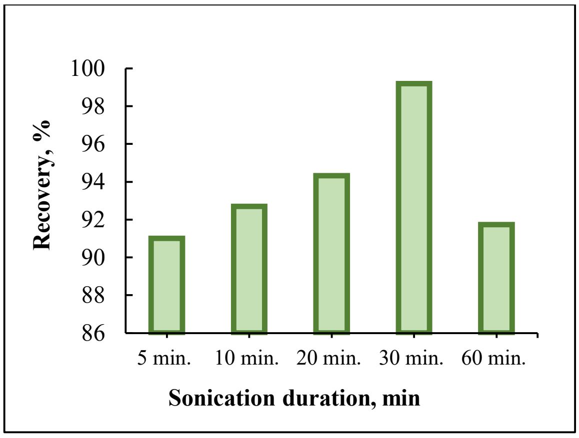

Fig.9. Time screening for NiO Nanoflower for Pb^{2+} recovery

3.3 Application of NiO nanoflowers enrichment to real samples

The optimum conditions obtained for Pb^{2+} with NiO nanoflower were applied to real wastewater and spinach samples and analyzed by FAAS. The results are given in Table 1.

For NiO nanoflower, close to 100% recovery was achieved in real samples (wastewater and spinach leaves). It is predicted that the method is suitable for the removal of a toxic element such as lead and NiO nanoflower can be used for filtration purposes.

Table 1. Analysis results on real samples (N=3)

	Added, mg/L	Pb^{2+}	Recovery, %
Wastewater	0	0.006 ± 0.002	-
	0.1	0.107 ± 0.011	101
	0.5	0.515 ± 0.036	102
Spinach leaves	0	0.2	-
	0.1	0.399 ± 0.02	99
	0.5	0.701± 1.2	100

4. Conclusion

Nanoflower-like NiO structures were synthesized by hydrothermal method in the presence of environmentally friendly solvents and used as an adsorbent for heavy metal Pb^{2+} removal. This adsorbent, which is suitable for many modifications depending on its surface morphology, can also allow the extraction of many other pollutants with high performance. NiO nanoflowers show that they can be efficient and environmentally friendly adsorbents for the removal of lead and other heavy metal ions from aqueous systems due to their high adsorption capacity, easy synthesis and relatively low production costs.

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