# Separation and preconcentration of lead(II), cobalt(II), and nickel(II) on EDTA immobilized activated carbon cloth prior to flame atomic absorption spectrometric determination in environmental samples

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**Abstract:** The synthesis and characterization of ethylenediaminetetraacetic acid immobilized activated carbon cloth was performed in the present work. It was used for preconcentration-separation of lead(II), cobalt(II), and nickel(II) at trace levels as an adsorbent. Factors including pH, concentration and volume of eluent, sample and eluent flow rates, sample volume, and effect of coexisting ions on the solid phase extraction of analytes were examined. The preconcentration factor was 50. The detection limits for Pb(II), Co(II), and Ni(II) were 4.39, 0.99 and 0.91 $\mu$g L$^{-1}$, respectively. The adsorption capacity for Pb(II), Co(II), and Ni(II) ions was found as 11.0, 11.2, and 10.2 mg g$^{-1}$, respectively. The validation of the method was performed by the analysis of certified reference materials (SPS-WW2 wastewater and BCR-146R sewage sludge amended soil (industrial origin)). The method was successfully applied for the determination of lead, cobalt, and nickel in fertilizer and water samples from Kayseri, Turkey.

**Key words:** EDTA modified activated carbon cloth, metal, preconcentration, adsorption, flame atomic absorption spectrometry

## 1. Introduction

Heavy metal pollution is a serious concern for ecology.[1,2] Heavy metals have accumulated in the environment, threatening our health, because of the increasing use of metal containing compounds and metal production in industry.[3−5] The determinations of heavy metals have been receiving much attention because of environmental problems and public health studies.[6−9] The direct determination of heavy metals at trace level by instrumental methods including inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), and flame and graphite atomic absorption spectrometry (AAS) is still problematic, because of their low concentrations in the samples and the complex matrix that interferes in the determination of analytes.[10−15] The separation and preconcentration techniques for trace metal ions are liquid-liquid extraction (LLE),[16] coprecipitation,[17] cloud point extraction (CPE),[18] and solid phase extraction (SPE),[19] which are used to solve these problems of trace metal determinations.

SPE methods are considered superior to other techniques for their simplicity, consumption of small volumes of organic solvent, and ability to obtain a high preconcentration factor and high speed.[19−21] SPE combined

with analytical instrumental techniques is an extensively used tool for accurate and precise determination of metal ions at very low concentrations in various samples.[22−24] A variety of new adsorbents that have high capacity, selectivity, and regenerability have been produced by researchers.[25−27] Activated carbon cloth (ACC) provides a higher surface area, special surface structure, excellent adsorption properties, and applicability to analytes with a wide spectrum of polarity. These excellent properties of ACC make it an attractive sorbent.[28−32]

Ethylenediaminetetraacetic acid (EDTA) is an important chelating agent for many metal ions.[33−35] It has also been used for separation-preconcentration works for metal ions at trace levels.

The present work describes a method for the separation and preconcentration of trace lead, cobalt, and nickel ions using EDTA immobilized ACC, which was characterized by using FT-IR, SEM, and BET methods. The effects of the pH, concentration, and volume of eluent; sample and eluent flow rates; and sample volume on quantitative separation-preconcentration of lead, cobalt, and nickel ions were investigated.

## 2. Results and discussion

### 2.1. Characterization of EDTA-ACC

FT-IR spectra for the ACC-COOH (A) and EDTA-ACC (B) are shown in Figure 1. For ACC-COOH, the FT-IR spectrum shows typical bands at 3085.84 and 1615.03 cm$^{-1}$ due to OH stretching vibration of COOH (carboxyl group) and C=O stretching and –OH bending vibration of COOH (carboxyl group). When ACC-COOH was modified by EDTA, several new peaks appeared in the spectrum. The new peaks can be assigned as follows: the peaks at 3114.29 cm$^{-1}$, 2919.43 cm$^{-1}$, 2850.99 cm$^{-1}$, 1500.00 cm$^{-1}$, 1186.17 cm$^{-1}$, 1057.29 cm$^{-1}$, 886.87 cm$^{-1}$, and 790.49 cm$^{-1}$. These peak values are due to –OH bending vibration of COOH (carboxyl group), -CH$_2$-asymmetric stretching vibration, -CH$_2$-symmetric stretching vibration, C-N stretching and N-H bending stretching vibrations, C-O stretching vibration, and C-H bending stretching vibrations, respectively.[36]

The SEM micrographs in Figures 2a and Figure 2b show a distinct change of the ACC. The regular fiber
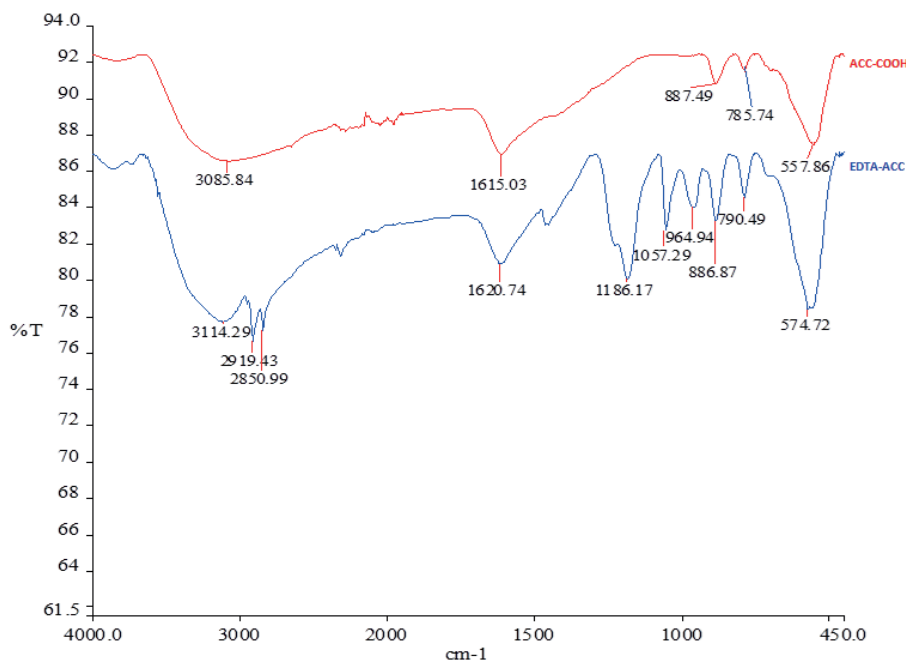


**Figure 1.** The FT-IR spectra of the ACC-COOH and EDTA-ACC.

structure of the ACC was corrupted because of the formation of ACC-COOH and gaps between the fibers were formed. This causes an increase in the surface in heterogeneity. Thus, the heterogeneity offers an advantage for the adsorption of the analytes in the gaps. The average diameter of the ACC fibers was measured by using SEM and found within the range of 5.2–6.9 $\mu$m (Figure 2).



(a)  (b)
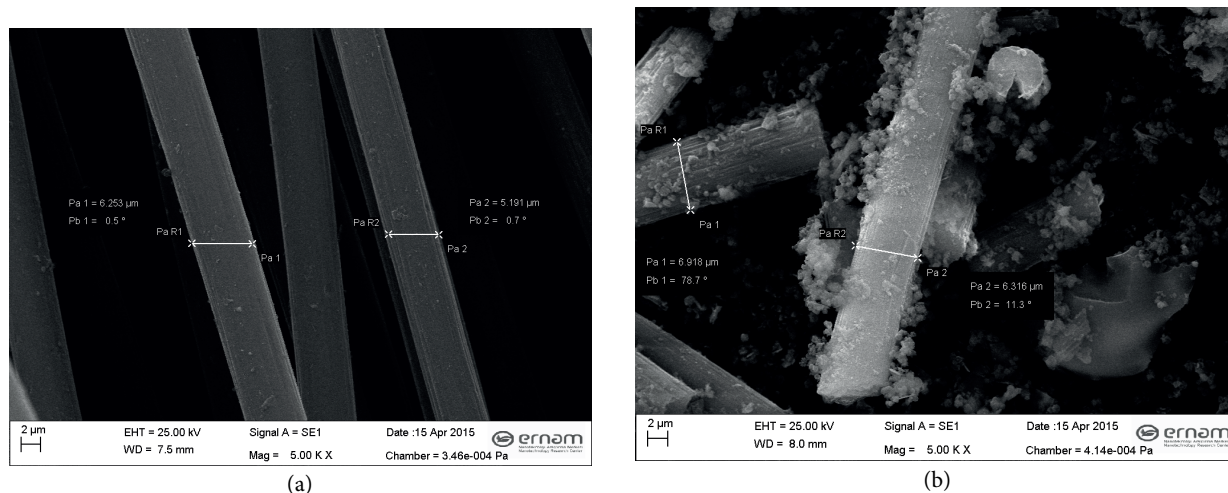
**Figure 2.** SEM images of the ACC (A) and EDTA-ACC (B).

The pore diameter, pore volume, and specific surface area were determined using nitrogen adsorption/desorption isotherm and single-point BET analysis. The BET isotherm of ACC-EDTA in Figure 3 shows that the contribution of mesopores to the total surface area and pore volume is significantly higher than that of macropores.[37] The pore diameter, pore volume, and surface area were found to be 3.38 nm, 0.303 cm$^3$ g$^{-1}$, and 1276 m$^2$ g$^{-1}$, respectively.

## 2.2. Optimization of the analytical parameters

All optimization works were performed by using model solutions that contain analyte ions. The recovery % value for analyte ions was calculated using the following relationship:

$$\text{Recovery } \% = (w_o/w_f) \times 100,$$

where w$_o$ ($\mu$g) is the amount of analyte in the final solution and w$_f$ ($\mu$g) is the amount of analyte in the beginning solution, respectively.

### 2.2.1. Effect of pH

pH is one of the critical parameters in solid phase extraction studies.[38−40] The pH of sample solution was studied within the range of 2.0–7.0 using buffer solutions. The effect of pH on the recoveries is shown in Figure 4. The quantitative extractions of Pb(II), Co(II), and Ni(II) ions were observed within the pH range of 4.0–5.0. For further investigations, all samples were buffered to pH 4.0.
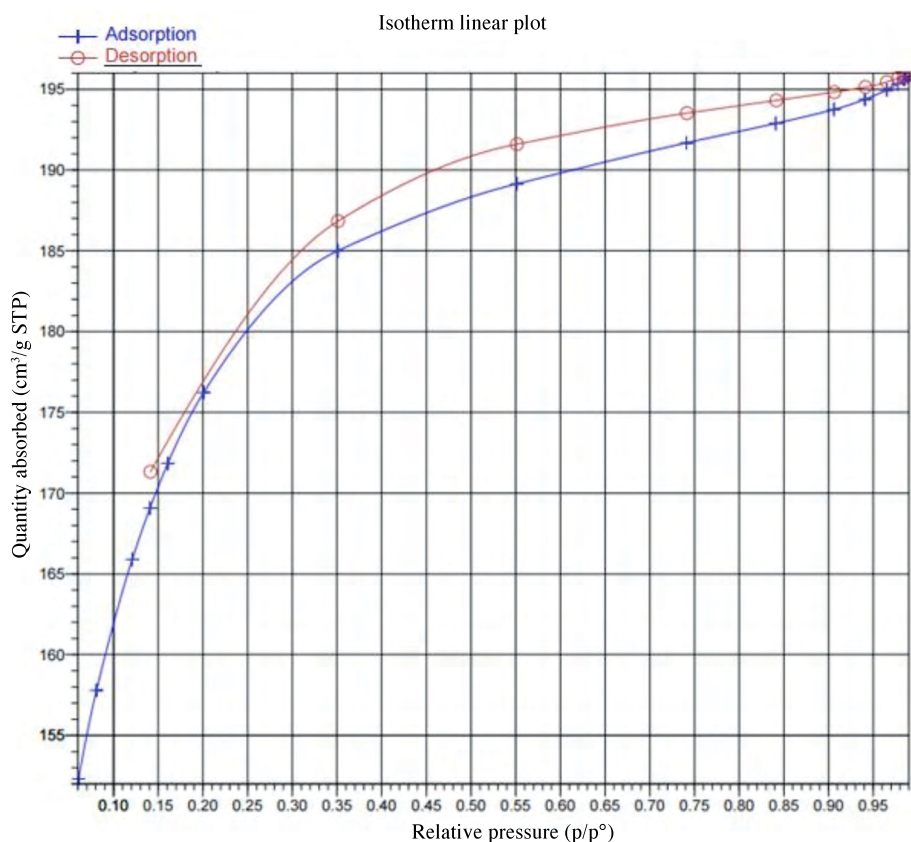
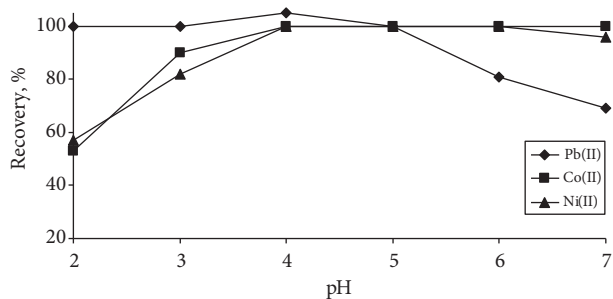**Figure 3.** Nitrogen adsorption/desorption isotherm of the EDTA-ACC.



**Figure 4.** Effect of pH on the recoveries of Pb(II), Co(II), and Ni(II) (N = 3).

The recoveries of analytes ions with unmodified ACC at pH 4 were 88% for lead, 83% for nickel, and 74% for cobalt. These values were not quantitative. These results show that for quantitative recoveries, modification of ACC is necessary.

### 2.2.2. Effect of elution conditions on the recovery

Different eluent types were used to desorb the Pb(II), Co(II), and Ni(II) ions from the EDTA-ACC. The results are given in Table 1. It was found that 3 mol $L^{-1}$ $HNO_3$ was sufficient for the quantitative elution ($>95\%$) of analyte ions. To find out the required eluent volume to recover all the analytes from EDTA-ACC, eluent volumes in the range of 4–13 mL were tested. Quantitative recoveries were obtained for all the analyte ions

with 10.0 mL of 3 mol $L^{-1}$ $HNO_3$ (Figure 5), and 10.0 mL of 3 mol $L^{-1}$ $HNO_3$ was selected as an eluent to achieve complete elution of the analyte ions.

**Table 1.** Effects of various eluents on the recoveries of Pb(II), Co(II), and Ni(II) (N = 3).
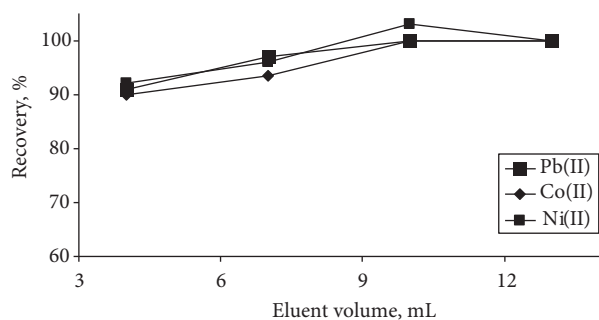
| Eluent type | Eluent concentration | Recovery, % | | |
|---|---|---|---|---|
| | | Pb(II) | Co(II) | Ni(II) |
| HNO$_3$ | 2 M | < 25 | 103 ± 4 | 105 ± 0 |
| | 3 M | 100 ± 0 | 105 ± 3 | 102 ± 4 |
| HCl | 2 M | 71 ± 3 | 100 ± 5 | 99 ± 2 |
| | 3 M | 100 ± 7 | 95 ± 0 | 91 ± 0 |
| CH$_3$COOH | 2 M | 79 ± 2 | 71 ± 4 | 53 ± 4 |
| | 3 M | 104 ± 2 | 88 ± 5 | 64 ± 4 |

Flow rate of the eluent solution was also optimized. For this purpose, different flow rates in the range of 1.0–5.0 mL $min^{-1}$ were checked with 10.0 mL of 3 mol $L^{-1}$ $HNO_3$. The quantitative recoveries were obtained at flow rates of 3.0 mL $min^{-1}$.

### 2.2.3. Effect of sample flow rate and sample volume

To investigate the effect of flow rate of the sample solution on the recovery, extraction experiments were carried out at flow rates in the range of 1.0–5.0 mL $min^{-1}$. It was found that the recoveries of analyte ions are quantitative up to 4 mL $min^{-1}$. A flow rate of 4.0 mL $min^{-1}$ was selected in order to obtain both maximum recovery and high speed.

The effects of sample volume on the recovery of the analytes were also investigated. The results are given in Figure 6. The recoveries of analytes were not affected until 500 mL of sample volume. Above 500 mL, the recoveries decreased for the analytes.



**Figure 5.** Effect of the eluent volume on the recoveries of Pb(II), Co(II), and Ni(II) (N = 3, eluent: 3.0 mol $L^{-1}$ $HNO_3$).
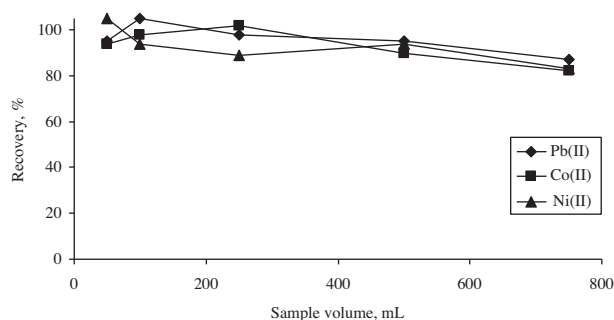
**Figure 6.** Effect of the sample volume on the recoveries of Pb(II), Co(II), and Ni(II) (N = 3).

Preconcentration factor is calculated by the ratio of highest sample volume (500 mL) that obtained quantitative recoveries (>95%) and final eluent volume (10 mL). Preconcentration factor was 50. The enhancement factor was defined as the ratio of the calibration curve slopes for analytes before and after the enrichment step. The enhancement factors were 41 for lead, 51 for nickel, and 49 for cobalt.

## 2.2.4. Effect of matrix ions

The effects of alkaline, earth alkaline, and anionic ions are an important problem in the flame atomic absorption spectrometric determinations of metals at trace levels.[22,41−46] The effects of matrix ions on the recoveries of Pb(II), Co(II), and Ni(II) ions on EDTA modified ACC were also investigated to verify the selectivity of the method for the preconcentration and separation of Pb(II), Co(II), and Ni(II) ions. A 50 mL solution, which contained different concentrations of other ions, was prepared and subjected to the developed method. The results are listed in Table 2. The recoveries for analyte ions were quantitative and satisfactory in the presence of most foreign ions at the level given in Table 2. The developed SPE method can be used for the determination of lead, cobalt, and nickel in real samples without any interference of the ions listed in Table 2.

**Table 2.** Influences of some foreign ions on the recoveries Pb(II), Co(II), and Ni(II) (N = 3).

| Ion | Added as | Concentration, mg L$^{-1}$ | Pb(II) | Co(II) | Ni(II) |
|---|---|---|---|---|---|
| Na$^+$ | NaNO$_3$ | 1000 | 100 $\pm$ 0 | 100 $\pm$ 2 | 101 $\pm$ 5 |
| K$^+$ | KCl | 1000 | 97 $\pm$ 5 | 96 $\pm$ 9 | 95 $\pm$ 4 |
| Mg$^{2+}$ | Mg(NO$_3$)$_2$.6H$_2$O | 500 | 100 $\pm$ 2 | 100 $\pm$ 2 | 101 $\pm$ 5 |
| Ca$^{2+}$ | Ca(NO$_3$)$_2$.4H$_2$O | 500 | 100 $\pm$ 2 | 100 $\pm$ 2 | 101 $\pm$ 5 |
| Mn$^{2+}$ | Mn(NO$_3$)$_2$.6H$_2$O | 20 | 97 $\pm$ 5 | 104 $\pm$ 0 | 100 $\pm$ 7 |
| Zn$^{2+}$ | Zn(NO$_3$)$_2$.6H$_2$O | 20 | 92 $\pm$ 5 | 100 $\pm$ 0 | 105 $\pm$ 7 |
| Cl$^-$ | KCl | 1000 | 97 $\pm$ 5 | 96 $\pm$ 9 | 95 $\pm$ 4 |
| SO$_4^{2-}$ | Na$_2$SO$_4$ | 500 | 97 $\pm$ 5 | 96 $\pm$ 0 | 95 $\pm$ 0 |
| PO$_4^{3-}$ | Na$_3$PO$_4$ | 500 | 100 $\pm$ 0 | 104 $\pm$ 0 | 100 $\pm$ 0 |
| NO$_3^-$ | NaNO$_3$ | 300 | 100 $\pm$ 0 | 96 $\pm$ 8 | 94 $\pm$ 4 |

## 2.3. Analytical performance

The analytical performance of the method, including the limits of detection (LOD), limits of quantification (LOQ), relative standard deviations (RSD, %), and preconcentration factors (PF), was calculated and is given in Table 3. The detection limits of the analytes were defined as 3 times the signal/slope (slope of calibration curve), whereas the quantification limits were defined as 10 times the signal/slope (slope of calibration curve). The relative standard deviations (RSD, %) for the analytes were evaluated using the results of the analysis of seven replicates containing 100 $\mu$g L$^{-1}$ Pb(II), Co(II), and Ni(II). The cycle results show that the adsorbent is stable for up to 100 runs without a decrease in the recoveries of analytes, and it can be reused.

**Table 3.** Analytical characteristics and adsorption isotherm capacity results of the method.

| Variables | Pb(II) | Co(II) | Ni(II) |
|---|---|---|---|
| LOD, $\mu$g L$^{-1}$ | 4.39 | 0.99 | 0.91 |
| LOQ, $\mu$g L$^{-1}$ | 14.5 | 3.27 | 3.02 |
| PF | 50 | 50 | 50 |
| RSD, % | 8.9 | 2.7 | 4.5 |
| Calibration curve | A = 6 $\times$ 10$^{-4}$ + 7.3 $\times$ 10$^{-3}$ C | A = 0.001 + 2.8 $\times$ 10$^{-2}$ C | A = −2.6 $\times$ 10$^{-3}$ + 3.2 $\times$ 10$^{-2}$ C |
| r$^2$ | 0.996 | 0.999 | 0.997 |
| q$_e$, mg g$^{-1}$ | 11.0 | 11.2 | 10.2 |
| K | 0.27 | 0.17 | 0.27 |
| n | 1.05 | 1.03 | 1.23 |

A = Absorbance value obtained by FAAS.

C = Concentration of analyte, $\mu$g mL$^{-1}$.

## 2.4. Adsorption isotherms and adsorption capacity

The adsorption capacity of the adsorbent was obtained by using the Freundlich isotherm based on the following equation:[47]

$$\ln q_e = \ln K + (1/n)\ln C_e, \tag{1}$$

where $C_e$ (mg L$^{-1}$) is the concentration of analytes in solution at equilibrium and $q_e$ (mg g$^{-1}$) is the amount of adsorbed analytes per gram of adsorbent at equilibrium (mg g$^{-1}$). $K$ and $n$ are Freundlich constants related to adsorption capacity and intensity, respectively. The slope and intercept of linear plots of ln $q$e against ln $C$e yield the values of $1/n$ and ln $K$ for Eq. (1). Figure 7 shows the adsorption isotherm, which conforms to the Freundlich isotherm. The obtained results for adsorption capacities and Freundlich constants for Pb(II), Co(II), and Ni(II) ions are given Table 3.
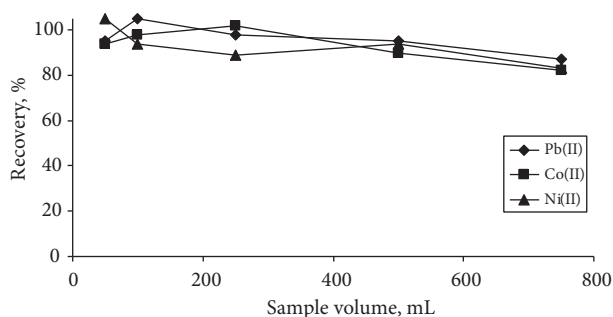


**Figure 7.** Freundlich adsorption isotherm models for Pb(II), Co(II), and Ni(II) adsorption on EDTA-ACC.

## 2.5. Applications

To evaluate the accuracy of the developed preconcentration method, certified reference materials (SPS-WW2 wastewater and BCR-146R sewage sludge amended soil (industrial origin)) were analyzed. The results are given Table 4. The results for certified reference materials show that the results are in good agreement with the certified values.

**Table 4.** The application of the presented method to certified reference materials.

| SPS-WW2 wastewater | Found, $\mu$g L$^{-1}$ | Certified value, $\mu$g L$^{-1}$ | Recovery, % |
|---|---|---|---|
| Pb | 490 ± 28 | 500 ± 3 | 98 |
| Co | 284 ± 8 | 300 ± 2 | 95 |
| Ni | 4860 ± 122 | 5000 ± 25 | 97 |
| BCR-146R sewage sludge amended soil (industrial origin) | Found, $\mu$g g$^{-1}$ | Certified value, $\mu$g g$^{-1}$ | Recovery, % |
| Pb | 532 ± 13 | 583 ± 17 [a] | 91 |
| Co | 6.2 ± 0.5 | 6.5 ± 0.4 [a] | 95 |
| Ni | 68.7 ± 0.0 | 65.0 ± 3.0 [a] | 106 |

[a]Aqua regia soluble content for certified reference material.

The addition-recovery method was applied to water and fertilizer samples. The tests of addition/recovery in the experiments for analyte ions were performed for dam water and fertilizer samples (Table 5). A reasonable agreement was obtained between the added and measured analyte amounts. The obtained results for analysis

of certified reference material and addition/recovery tests show that the proposed method was helpful for the determination of lead, cobalt, and nickel in real samples with complicated matrices.

**Table 5.** Tests of addition/recovery for fertilizer and dam water samples (N = 3).

| | | Fertilizer | | | Dam water | |
|---|---|---|---|---|---|---|
| | Added, $\mu$g | Found, $\mu$g | Recovery, % | Added, $\mu$g | Found, $\mu$g | Recovery, % |
| Pb(II) | 0.0 | BDL[a] | - | 0.0 | BDL | - |
| | 10.0 | $10.1 \pm 1.3$ | 101 | 20.0 | $19.1 \pm 1.0$ | 96 |
| | 30.0 | $29.2 \pm 1.9$ | 97 | 40.0 | $38.1 \pm 0.0$ | 95 |
| Co(II) | 0.0 | $16.6 \pm 1.5$ | - | 0.0 | BDL | - |
| | 10.0 | $27.8 \pm 0.0$ | 105 | 20.0 | $19.4 \pm 0.5$ | 97 |
| | 30.0 | $48.4 \pm 1.1$ | 105 | 40.0 | $38.1 \pm 0.7$ | 95 |
| Ni(II) | 0.0 | $14.3 \pm 1.5$ | - | 0.0 | BDL | - |
| | 10.0 | $23.9 \pm 1.0$ | 98 | 20.0 | $20.2 \pm 0.9$ | 101 |
| | 30.0 | $46.4 \pm 1.2$ | 105 | 40.0 | $36.4 \pm 0.6$ | 91 |

[a]Below the detection limit.

Different water samples and liquid fertilizer samples were subjected to the developed preconcentration and separation method for determination of concentrations of lead, cobalt, and nickel. The results are given in Table 6.

**Table 6.** Determination of lead, cobalt, and nickel in water and fertilizer samples (N = 3).

| Sample | Concentration ($\mu$g mL$^{-1}$) | | |
|---|---|---|---|
| | Pb | Ni | Co |
| Wastewater 1 | BDL [a] | $39.3 \pm 1.6$ [b] | BDL |
| Wastewater 2 | BDL | $0.40 \pm 0.01$ | BDL |
| Well water | BDL | BDL | BDL |
| Fertilizer-II | $0.34 \pm 0.05$ | $0.20 \pm 0.01$ | $0.13 \pm 0.03$ |
| Fertilizer-III | BDL | $0.25 \pm 0.01$ | BDL |
| Fertilizer-IV | BDL | BDL | BDL |

[a]BDL: Below the detection limit.
[b]Mean $\pm$ standard deviation.

## 2.6. Conclusions

EDTA impregnated ACC has been prepared, characterized, and applied to the solid phase extraction and preconcentration of lead, cobalt, and nickel prior to their determination by FAAS. It was found that the EDTA-ACC can efficiently adsorb the lead, cobalt, and nickel from water solutions predominantly by interactions between metal ions and EDTA-ACC. The functionalization of ACC with EDTA causes an increase in the surface in the heterogeneity of the ACC and hence increases the adsorption capacity. The recoveries of analyte ions were virtually quantitative and were unaffected by matrix components. The developed SPE method displayed detection limits comparable to or better than those of other SPE methods[48−58] developed for the determination of Pb(II), Ni(II), and Co(II) in different samples (Table 7), with good relative standard deviations and high preconcentration factors. The proposed preconcentration/separation method could be applied to highly saline samples.

**Table 7.** Comparison of this SPE method with other SPE methods for the determination of lead, nickel, and cobalt in real samples with FAAS.

| Instrument | Limit of detection, $\mu$g L$^{-1}$ | Sample | Ref. |
|---|---|---|---|
| FAAS | Pb: 22.5, Ni: 2.9, Co: 0.95 | Water | 48 |
| FAAS | Pb: 0.60, Ni: 0.57, Co: 0.40 | Food and environmental samples | 49 |
| FAAS | Pb: 0.121, Ni: 0.161, Co: 0.072 | Water | 50 |
| FAAS | Pb: 0.60, Ni: 0.44, Co: 0.25 | Water, wine, and food | 51 |
| FAAS | Pb: 25, Ni: 7.5 | Water | 52 |
| FAAS | Pb: 7.2, Ni: 4.3 | Food | 53 |
| FAAS | Pb: 3.52, Ni: 5.68, Co: 5.31 | Environmental samples | 54 |
| FAAS | Pb: 4.39, Ni: 0.91, Co: 0.99 | Fertilizer and water | This study |

## 3. Experimental

### 3.1. Chemicals and solutions

All solutions were prepared with reverse osmosis purified water (18.2 M$\Omega$ cm, Millipore). All of the reagents and solvents were of analytical reagent grade and used as received. The stock solutions (1000 mg/L) of Pb(II), Co(II), Ni(II), and other cations were prepared by dissolving the appropriate amounts of nitrate salts of elements in reverse osmosis purified water.

The ACC was purchased from Norm Company, Turkey (Code: Norm/AW1105). It has a surface area and thickness of 1000 m$^2$ g$^{-1}$ and 0.4 $\pm$ 0.1 mm, respectively. Three buffer solutions were prepared: (a) from 0.25 mol L$^{-1}$ phosphoric acid and 0.25 mol L$^{-1}$ sodium dihydrogen phosphate solution for pH 3.0, (b) from 0.25 mol L$^{-1}$ ammonium acetate solution and acetic acid for pH 4.0–5.0, (c) from 0.25 mol L$^{-1}$ sodium dihydrogen phosphate solution and 0.25 mol L$^{-1}$ disodium hydrogen phosphate solution for pH 6.0–7.0. SPS-WW2 wastewater (Spectrapure Standards AS, Oslo, Norway) and BCR-146R sewage sludge amended soil (EC-JRC-IRMM, Retieseweg, Belgium) certified reference materials were used.

### 3.2. Instruments

The FT-IR spectra were recorded on a PerkinElmer Spectrum 400 FT-IR spectrometer (Waltham, MA, USA). SEM images were obtained on a Zeiss EVOLS 10 with an accelerating voltage of 20 kV. The surface area, pore volume, and pore size of EDTA-ACC were determined by the BET-N$_2$ method using a Micromeritics Gemini VII analyzer.

A PerkinElmer Model 3110 flame atomic absorption spectrometer (FAAS; Norwalk, CT, USA) was used for determination of analyte elements. All instrumental settings were those recommended in the manufacturer's manual. All measurements were carried out with an air/acetylene flame.

### 3.3. Synthesis of EDTA modified ACC

One gram of ACC was first oxidized by using 200 mL of conc. HNO$_3$ for 24 h at 50 °C. The product was then filtered and washed with water until pH 7. The ACC-COOH was dried overnight in an oven at 70 °C. One gram of the dry ACC-COOH was reacted with 50 mL of 5% (v/v) thionyl chloride (SOCl$_2$) in toluene for 3 h at 70 °C, and then the SOCl$_2$ was removed by rotary evaporator and the product was washed 3 times with ethanol. The produced ACC-COO-Cl was refluxed with 50 mL of 1% EDTA. The product was filtered and washed with ethanol and water respectively to remove the unreacted species. The produced adsorbent EDTA-ACC was dried overnight in the oven at 70 °C.

### 3.4. Procedure

EDTA-ACC (0.4 g) was filled into a glass column with a porous disk (10 cm long and 1.0 cm in diameter). Then, for column pretreatment, 4 mL of 3 M $HNO_3$, 4 mL of water, and 4 mL of pH 4.0 buffer solutions at 4 mL min$^{-1}$ were passed through the column system for 3 min, respectively. The pH of model solutions containing analyte ions was adjusted to pH 4.0. After 5–10 min, the solution was loaded into the EDTA-ACC column. The solution was then passed through the column at 4 mL min$^{-1}$ under gravity. After the passage of the solution finished, the column was washed with 20 mL of water. The metal ions retained on the column were eluted with 20 mL of 3 mol L$^{-1}$ $HNO_3$ elution solution at a flow rate of 3 mL min$^{-1}$. The determinations of concentrations of lead, nickel, and cobalt in eluent solution were conducted by FAAS.

### 3.5. Adsorption capacity

In order to find the adsorption capacities of the EDTA-ACC, the analyte ions were added to 100 mL of synthetic model solution at increasing concentrations of Pb (5–50 $\mu$g mL$^{-1}$) and Co and Ni (5.0–200 $\mu$g mL$^{-1}$). Ten minutes was enough to reach equilibrium conditions. The developed SPE method given in Section 3.4 was applied to these samples at room temperature at 4 mL min$^{-1}$ under gravity. The eluent solution was diluted between 10-fold and 100-fold. The concentration of analyte ions in the eluent was determined by FAAS.

### 3.6. Analysis of real samples

Dam water from Kayseri, a wastewater sample from the Kayseri Organized Industrial Area, and well water from Ankara, Turkey, were collected in prewashed polyethylene containers and filtered through a Millipore cellulose membrane filter (0.45 $\mu$m pore size). Then the developed SPE method given in Section 3.4 was applied to these water samples and a water certified reference material (SPS-WW2 wastewater)

The method was also applied to BCR-146R sewage sludge amended soil (industrial origin) certified reference material and fertilizer samples. One gram of dry certified reference material or fertilizer was put into beakers, and then 30 mL of aqua regia was added to the beaker. The contents of the beaker were evaporated to near dryness on a hot plate at about 120 °C. The step was replicated two times to near dryness. After that, the samples were filtered and diluted, and the method was applied.

The method given in Section 3.4 was applied to three kinds of liquid fertilizer samples obtained from Çanakkale, Turkey. The analytes in eluate were determined with flame AAS.

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