



Chelating agent free-solid phase extraction (CAF-SPE) of Co(II), Cu(II) and Cd(II) by new nano hybrid material (ZrO_2/B_2O_3)

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ARTICLE INFO

Article history:

Received 17 May 2011

Received in revised form 15 August 2011

Accepted 15 August 2011

Available online 22 August 2011

Keywords:

Nanosorbent

Flame atomic absorption spectrometry

Preconcentration

Boron oxide

Zirconia

Heavy metal

ABSTRACT

New nano hybrid material (ZrO_2/B_2O_3) was synthesized and applied as a sorbent for the separation and/or preconcentration of Co(II), Cu(II) and Cd(II) in water and tea leaves prior to their determination by flame atomic absorption spectrometry. Synthesized nano material was characterized by scanning electron microscope, transmission electron microscope and X-ray diffraction. The optimum conditions for the quantitative recovery of the analytes, including pH, eluent type and volume, flow rate of sample solution were examined. The effect of interfering ions was also investigated. Under the optimum conditions, adsorption isotherms and adsorption capacities have been examined. The recoveries of Co(II), Cu(II) and Cd(II) were $96 \pm 3\%$, $95 \pm 3\%$, $98 \pm 4\%$ at 95% confidence level, respectively. The analytical detection limits for Co(II), Cu(II), and Cd(II) were 3.8, 3.3, and $3.1 \mu\text{g L}^{-1}$, respectively. The reusability and adsorption capacities (32.2 mg g^{-1} for Co, 46.5 mg g^{-1} for Cu and 109.9 mg g^{-1} for Cd) of the sorbent were found as satisfactory. The accuracy of the method was confirmed by analyzing certified reference material (GBW-07605 Tea leaves) and spiked real samples. The method was applied for the determination of analytes in tap water and tea leaves.

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1. Introduction

The accurate determination of trace elements in environmental samples is an important and challenging task in analytical chemistry. Direct determination of trace elements appears to be difficult task as the concentration of them is close to or below the detection limits of most of the analytical techniques besides the real sample matrix may cause serious interference during their determination process. However, these problems can be solved by applying the preconcentration techniques which can simultaneously remove the sample matrix and increase the concentration of analytes [1,2].

Various preconcentration methods including liquid–liquid extraction [3,4], ion exchange [5,6], co-precipitation [7,8], flotation [9], cloud point extraction [10,11] and solid phase extraction [12–17] have been used to remove the sample matrix and increase the concentration of analytes. Among the preconcentration techniques, solid phase extraction (SPE) technique has increasingly become a popular technique. It has several major advantages including operation simplicity, high preconcentration factor, minimum eluent volume, reduced disposal cost, shorter extraction time for sample preparation [18,19] and the availability of a wide

variety of sorbent materials that mainly affect the extraction efficiency. In the past decade, nanometer solid materials have become more and more important due to their special properties [20]. It is known that diameter of nanoparticles is less than 100 nm, and with the decrease in diameter the number of atom on the surface and surface area increases rapidly. Consequently, nano-meter sized materials can adsorb many ions and reach equilibrium in a very short time. Moreover, the adsorption ability of nano materials compared with other solid phase extractor is rather high [21]. Recently nano materials have been used as a sorbent due to their improved intrinsic properties such as chemical activity and fine grain size compared with classical sorbents (i.e., TiO_2 , Al_2O_3) [2,22,23]. Nano material can be prepared by various techniques such as chemical vapor deposition [24], and sol–gel method [25,26]. In recent years, many papers have been published for trace metal preconcentration by nano materials as sorbent which have been synthesized and used [27–34]. An actual tendency in the field of solid phase extraction is related to synthesis of the new sorbent materials with good performance, such as high resistance to acids and bases, selective for analytes, large surface area and high adsorption capacity [28]. To increase the performance of a sorbent it is usually modified with chelating agents or microorganisms. As a modification, chelating agents or microorganisms have been loaded or immobilized on a solid substrate [35,36]. However, the modification or chelating agent addition may cause an increase in

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possible contamination and interferences due to the reagents used for modification. The modification also limits repeated use of sorbent due to the loss of chelating agents or microorganisms from the solid sorbent. To minimize possible contaminations and interfering effects and to increase repeated use of sorbent, chelating agent or microorganism free solid phase extractors have also been proposed [29,37–39].

In this study, hybrid nano ZrO_2/B_2O_3 was synthesized as a new solid phase extractor and used without modification for the preconcentration of Co(II), Cu(II) and Cd(II). To the best of our knowledge this is the new solid phase extractor used for this purpose. This hybrid material was firstly synthesized by us and used for this purpose. The synthesized material was first characterized by using scanning electron microscope (SEM), transmission electron microscope (TEM) and X-ray diffraction (XRD) methods and then used as solid phase extractor. The procedure was validated by analyzing certified reference materials and applied for various real samples. In our previous paper [29], nano B_2O_3/TiO_2 composite material had been used as a new solid phase extractor for the preconcentration and separation of cadmium. In this study, ZrO_2/B_2O_3 was used for the preconcentration and separation of Co, Cu and also cadmium. These two materials have almost similar advantages for capturing heavy metals. The higher preconcentration factor was obtained for cadmium by using B_2O_3/TiO_2 material.

2. Experimental

2.1. Apparatus

A Technai G2 120 kV transmission electron microscope (Oregon, USA), a JEOL LV6060 model scanning electron microscope (Tokyo, Japan) with EDS apparatus and a BRUKER D8 discover X-ray diffractometer (Madison, USA) were used for the determination of morphology of the synthesized nano material. The experimental conditions of XRD measurement were as follows: $CuK\alpha$ 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, copper hollow cathode lamp (Varian), cadmium hollow cathode lamp (Varian), multi element (Co–Mo–Pb–Zn) hollow cathode lamp (Varian) and air acetylene flame as the atomizer was used for the determination of Co, Cu and Cd under the conditions suggested by the manufacturer. The wavelength, lamp current, slit width and acetylene flow rate were 240.7 nm, 7 mA, 0.2 nm and 2 L min⁻¹ for Co, 324.8 nm, 4.0 mA, 0.5 nm and 2 L min⁻¹ for Cu and 228.8 nm, 4 mA, 0.5 nm and 2 L min⁻¹ for Cd, respectively. A Varian AA240Z graphite furnace atomic absorption spectrometer was used for cadmium and cobalt determination in Certified Reference Material (GBW-07605) using the instrumental parameters given in Table 1. All pH measurements were made with a WTW 720 model pH meter (Weilheim, Germany).

2.2. Reagents and solutions

All reagents were of analytical grade, unless otherwise stated. All solutions were prepared in ultra pure water (18.3 $\mu S cm^{-1}$). Multi element standards (in various concentrations) and model solutions were prepared by dilution of single element stock solutions (1000 $\mu g mL^{-1}$) of Co(II), Cu(II) and Cd(II) ions purchased from Merck. $Zr(OC_2H_5)_4$ (BDH), ethanol (99.5%, J.T. Baker), $Al(NO_3)_3 \cdot 9H_2O$ (Merck), $NaNO_3$ (Carlo Erba), KNO_3 (Merck), $Ca(NO_3)_2 \cdot 4H_2O$ (J.T. Baker), $MgSO_4$ (Carlo Erba), $Ni(NO_3)_2 \cdot 6H_2O$ (Carlo Erba), HNO_3 (Merck, 65%), HCl (Merck, 37%), NH_3 (Merck, 27%) were used.

Table 1

Instrumental parameters of electrothermal atomic absorption spectrometry for Co and Cd.

Parameters	Values	
	Co	Cd
Sample volume (μL)	20	20
Lamp current (mA)	7	4
Argon flow rate ($mL min^{-1}$)	3	3
Drying 1, °C	95	95
Ramp time (s)	5	5
Hold time (s)	40	40
Drying 1, °C	120	120
Ramp time (s)	15	15
Hold time (s)	15	15
Pyrolysis, °C	750	300
Ramp time (s)	15	15
Hold time (s)	10	10
Atomization, °C	2300	1800
Ramp time (s)	1	1
Hold time (s)	3	3
Cleaning, °C	2500	2200
Ramp time (s)	1	1
Hold time (s)	2	2

2.3. Preparation of hybrid nano zirconium dioxide–boron oxide sorbent

Hybrid nano ZrO_2/B_2O_3 was synthesized by modifying the procedure given in the literature [28], given for nano alumina synthesis. For this purpose, 10 g of H_3BO_3 and 5 g of $Zr(OC_2H_5)_4$ were weighed into a beaker containing about 50 mL of ethanol. Then, 1.5 mL of Triton X-114 was added in the mixture as surfactant and stirred for 1 h. The mixture was sonicated for about 30 min in ultrasonic bath. pH of the mixture was adjusted to 6 and then sonication was applied again for 15 min. The mixture was left for 12 h at room temperature and then dried in an oven at 70 °C for about 1 h. The obtained solid material was then transferred into the muffle furnace and heated at 850 °C for about 2 h. Then, the material was ground in a Spex type ball mill to obtain powder product.

2.4. Column preparation

A glass column (150 mm length and 8 mm i.d.) having a stopcock at the bottom and a tank of 250 mL on top of the column was used. A small amount of glass wool was placed over its stopcock in order to hold the sorbent. 200 mg dry hybrid nano material (ZrO_2/B_2O_3) was made slurry in water and then placed into the column. Then, another small amount of glass wool was inserted onto the top of the sorbent to avoid disturbance of the adsorbent during sample passage. The column was preconditioned by passing blank solution having same pH with the sample solution prior to use. After each use, the nano material in the column was washed with dilute HCl (0.5 mol L⁻¹) and water, respectively and stored in water until the next experiment.

2.5. Preconcentration and determination procedure

The separation/preconcentration procedure based on the solid phase extraction via hybrid nano material (ZrO_2/B_2O_3) was tested with model sample solutions prior to the determination of analytes in real samples. For this purpose, 50 mL of solution containing 10 μg Co(II), 10 μg Cu(II) and 10 μg Cd(II) were taken and the pH was adjusted to the optimum value determined experimentally with dilute HCl (0.1 mol L⁻¹) or NH_3 (0.1 mol L⁻¹) solutions. The column was conditioned to the working pH by passing the aqueous solution having same pH value. Then the sample solution was passed through the column at a flow rate adjusted to the optimum value (5 mL min⁻¹) determined experimentally. The retained ana-

lytes on the sorbent were then eluted with 10 mL of 1 mol L⁻¹ HNO₃ solution. This solution was aspirated into an air-acetylene flame for the determination of analytes by FAAS. A blank solution was also run under the same conditions without adding the analytes. The nano ZrO₂/B₂O₃ sorbent was used repeatedly after washing with 1 mol L⁻¹ HNO₃ solution and distilled water, respectively. The recovery of analytes was calculated from the ratio of the concentration found by FAAS to that calculated theoretically.

2.6. Collection and preparation of samples

Tap water sample was collected from the laboratory of chemistry department. This water sample was filtered from blue ribbon filter paper.

Approximately 1.0 g of tea samples (Tea samples purchased from local market in the city of Ankara, Turkey and standard reference material, Tea leaves GBW-07605) were taken in a 250 mL beaker and 10 mL of concentrated nitric acid was added. The beaker was heated on a hot plate at about 130 ± 10 °C for 3 h. After cooling to room temperature, 2 mL of hydrogen peroxide was added drop wise. The beaker was heated until complete decomposition of tea sample. The resulting solution was transferred into a 50 mL volumetric flask by washing the interior surface of the beaker with small portions of ultra pure water, and the solution was diluted to the mark with ultra pure water.

3. Results and discussion

Firstly characterization of synthesized material has been performed to demonstrate the nano character and to determine crystalline structure of synthesized material. Then, the applicability of the material as a solid phase extractor has been tested in detail.

In order to obtain optimum separation and/or preconcentration conditions and maximum recoveries, some experimental parameters such as the pH of sample solution, type and concentration of eluent, volume of sample solution and flow rate of sample solution have been optimized. Interfering effects, reusability of hybrid sorbent and adsorption isotherms have also been studied. The analytical parameters such as limit of detection (LOD), limit of quantitation (LOQ), precision, accuracy and linear working range have been determined at optimal experimental conditions.

3.1. Characterization of synthesized material

The synthesized material was characterized by scanning electron microscope (SEM), transmission electron microscope (TEM) and X-ray diffraction (XRD) method. Firstly, it was investigated that whether the material has nano size or not. For this purpose, SEM and TEM images of the material were obtained. As can be seen from the SEM and TEM images of hybrid nano ZrO₂/B₂O₃ hybrid material (Figs. 1 and 2), the ZrO₂/B₂O₃ particles are very fine and the grain size is below 100 nm. From these results, it can be concluded that nano scale material, which is one of the purpose of this study, could be obtained by the method described above. Secondly, in order to characterize the nature of synthesized nano material, XRD pattern of the material was also investigated. According to the XRD pattern shown in Fig. 3, the nanoparticles are identified as crystalline B₂O₃ and ZrO₂. It can be seen that the synthesized new nano material consisted mainly of B₂O₃ and ZrO₂.

3.2. Effect of pH of sample solution

The pH value plays an important role in adsorption of the ions onto sorbents. It strongly influences the sorption availability of the metal ions. Therefore, pH was the first optimized parameter. The

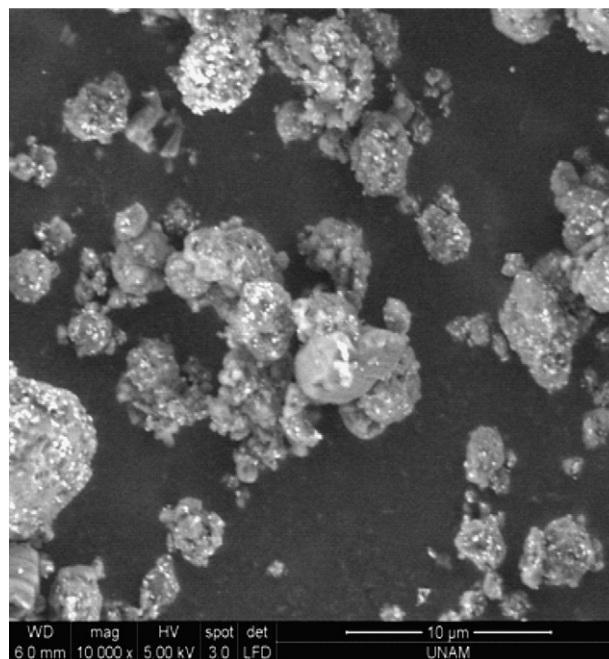


Fig. 1. SEM micrographs of synthesized hybrid nano ZrO₂/B₂O₃.

recovery of the analytes was determined by applying the general procedure (Section 2.5) by changing the pH of model solution in the range of 1–10. The variation in recovery of metal ions with pH is shown in Fig. 4. As can be seen, Co(II) and Cd(II) were quantitatively (above 95%) recovered at the pH range of 8–10 and Cu(II) was quantitatively recovered at the pH range 6–10. pH 8 is an appropriate pH for all of the analytes when they will be determined simultaneously. However, if they will be determined separately, as an optimum pH 8 should be selected for Co(II) and Cd(II) and 6 should be selected for Cu(II) due to advantages of acidic pH values. Hence, the following optimization work was carried out at these pHs.

3.3. Effect of eluent type and concentration

The type, amount, and concentration of eluent are other important parameters for this kind of studies. In order to determine type and amount of elution solution, 50 mL of model solutions contain-

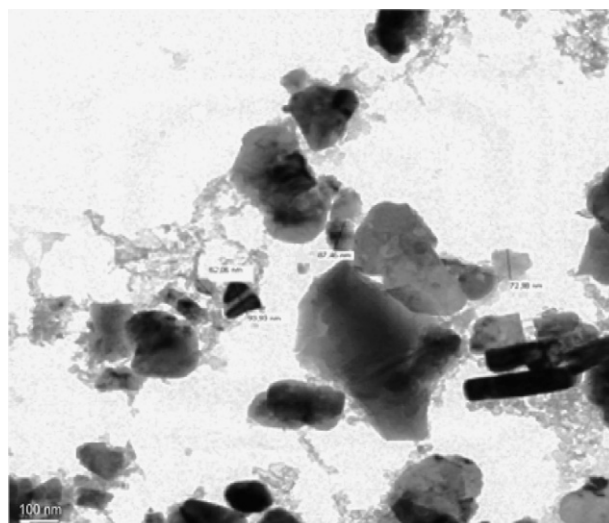


Fig. 2. TEM micrographs of synthesized hybrid nano ZrO₂/B₂O₃.

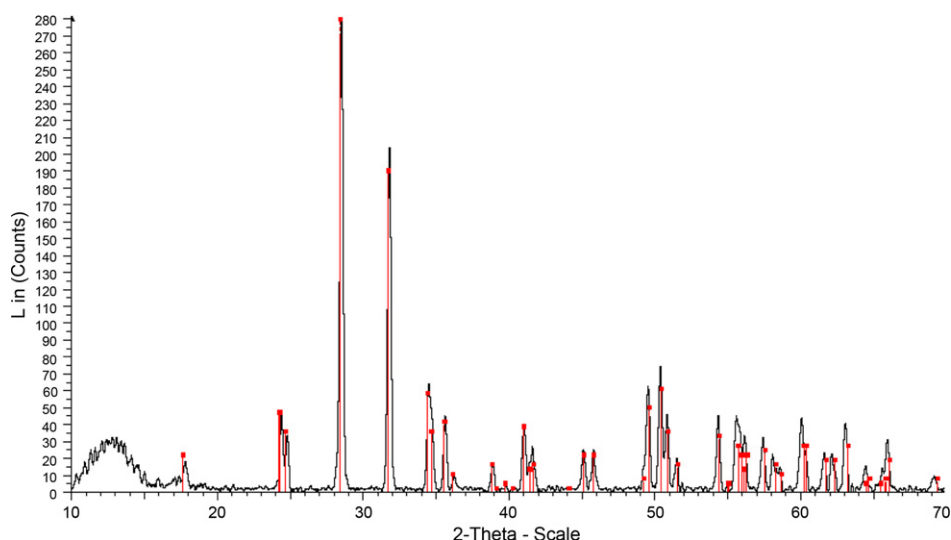


Fig. 3. XRD pattern of synthesized hybrid nano ZrO_2/B_2O_3 .

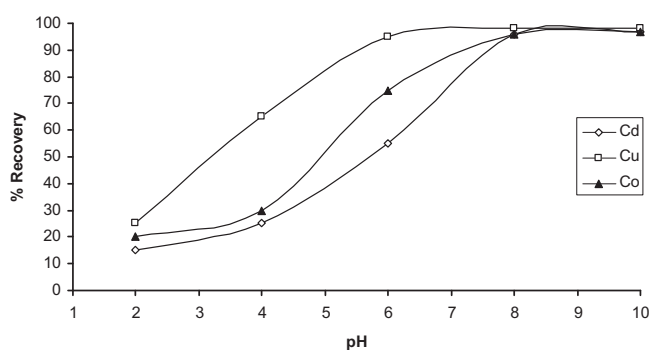


Fig. 4. Effect of pH of sample solution.

ing 10 μg Co(II), Cu(II) and Cd(II) were used. pH of the solutions was adjusted to 6 for Cu(II) and to 8 for Co(II) and Cd(II), and the general procedure was applied. For the elution process, HCl and HNO_3 solutions having various concentrations and various volumes were tested (Table 2). As a result of experiments, 10 mL of 1.0 mol L^{-1} HNO_3 and 10 mL of 2.0 mol L^{-1} HNO_3 solutions that give maximum recovery was found as optimum eluents. However, for subsequent experiments, 10 mL of 1.0 mol L^{-1} HNO_3 was used to desorption of Co(II), Cu(II) and Cd(II) from the column due to its lower concentration.

Table 2
The effect of eluent type and volume on the recovery of analytes.

Eluent type and volume	Recovery ^a (%)		
	Cd(II)	Cu(II)	Co(II)
10 mL 1 M HCl	95 ± 3	122 ± 6	87 ± 3
10 mL 2 M HCl	94 ± 4	118 ± 4	85 ± 4
10 mL 3 M HCl	95 ± 4	111 ± 5	93 ± 4
5 mL 1 M HCl	75 ± 5	75 ± 3	–
5 mL 2 M HCl	78 ± 5	78 ± 4	–
5 mL 3 M HCl	80 ± 4	80 ± 4	–
10 mL 0.5 M HNO_3	91 ± 5	88 ± 3	83 ± 4
10 mL 1 M HNO_3	98 ± 4	99 ± 3	95 ± 3
10 mL 2 M HNO_3	98 ± 3	102 ± 3	97 ± 3
5 mL 1 M HNO_3	78 ± 4	72 ± 3	66 ± 4
5 mL 2 M HNO_3	82 ± 5	76 ± 4	71 ± 3

^a Mean of the three replicates.

3.4. Effect of the sample flow rate

The influences of flow rates of samples were investigated by controlling the flow rate of sample solution with peristaltic pump. The effect of flow rate of sample solutions on the recoveries of analytes was examined in the range of 1–10 mL min^{-1} . Under optimum conditions (pH: 6 for Cu(II) and 8 for Co(II) and Cd(II); eluent: 10 mL of 1.0 mol L^{-1} HNO_3), the analytes were quantitatively recovered up to 5 mL min^{-1} of the flow rates. Above 5 mL min^{-1} the recoveries were decreased gradually. Because the eluent volume was very low, the effect of flow rate of eluent has not been studied.

3.5. Effect of volume of sample solution

Another parameter investigated to find the best experimental conditions is the volume of sample solution and/or analyte concentration. In order to determine the maximum applicable sample solution (or minimum analyte concentration), the effect of the volume of sample solution on the recovery of the analytes were investigated by using model solutions and by applying general procedure mentioned in Section 2.5. For this purpose, Co(II), Cu(II) and Cd(II) were preconcentrated from sample volumes of 25, 50, 100, 150, 200 and 250 mL containing 10 μg Co(II), Cu(II) and Cd(II) corresponding to analyte concentration of 0.4, 0.2, 0.1, 0.067, 0.05 and 0.04 $\mu\text{g mL}^{-1}$, respectively.

The recovery of analytes were quantitative (>95%) for sample volumes up to 100 mL for Co and Cu and 150 mL for Cd. After the preconcentration of 150 mL for Cd and 100 mL for Co and Cu sample solution, if 10 mL of eluent solution was used for the analysis, the preconcentration factor was found to be 15 for Cd and 10 for Co and Cu. As a result, it can be concluded that 0.1 $\mu\text{g mL}^{-1}$ for Co(II) and Cu(II) and 0.067 $\mu\text{g mL}^{-1}$ for Cd(II) could be determined by applying this preconcentration method; that cannot be determined directly by FAAS with sufficient precision and accuracy.

3.6. Reusability of the sorbent

The stability and potential reusability of the sorbent were assessed by monitoring the change in the recoveries of the analytes through several adsorption–elution cycles. The passage of 100 mL of sample (containing 200 $\mu\text{g L}^{-1}$ analyte) solution, 10 mL of 1.0 mol L^{-1} HNO_3 and 50 mL of ultra pure water through the column packed with 200 mg of hybrid sorbent, respectively, was considered one adsorption–elution cycle. The adsorbent was always stored in

water when it was not in use. It was observed that the column could be reused up to 100 times without decrease in the recoveries of the analytes.

3.7. Influence of foreign ions

The preconcentration procedures and thus the recovery of trace metals may be affected by the other constituents of the samples. For this reason, the reliability of the proposed method should be examined in the presence of possible interfering ions of the samples. To investigate the effect of other constituent on the recovery of the analytes, the possible interfering elements were added to 50 mL of model solutions containing 10 µg Co(II), Cu(II) and Cd(II) ions as their nitrate or chloride salts. As the tolerance limit, ion concentration causing ±5% deviation in recovery of the analytes is considered. As can be seen from Table 3, foreign ions except Ni(II) have no significant effect on the recovery of analyte ions. The results show that above 1 mg L⁻¹ Ni(II) ions interfere with Co(II) signal. In the presence of Ni(II), absorbance of cobalt decreases significantly. Preliminary experiments show that Ni(II) can also be retained by the sorbent at pH 8 and can be eluted by same eluent. As a result, it can be concluded that the interfering effect does not occur in preconcentration process but it occurs during atomic absorption measurements. Therefore, in order to eliminate the Ni(II) interference on Co, atomization conditions were optimized. To dissociate inter-metallic compound that could be occur between Ni and Co, higher temperature flame, N₂O-acetylene flame which was proposed by the cookbook of the instrument, was used for Co(II) determination. By using N₂O-acetylene flame, the tolerance limit of Ni(II) increases up to 25 mg L⁻¹.

3.8. Adsorption isotherm and adsorption capacity

The adsorption isotherms were used to characterize the interaction of each analyte ions with the adsorbent. Among the several isotherm equations, Langmuir adsorption isotherm which is valid for monolayer adsorption onto a surface with a finite number of identical sites and based on the assumption of surface homogeneity such as equally available adsorption sites, and no interaction between adsorbed species [41], was investigated. Adsorption isotherm provides a relationship between the concentration of analyte ions in the medium and the amount of analyte ions adsorbed on the solid phase when the two phases are at equilibrium.

The adsorption isotherms and adsorption capacity of the synthesized nano hybrid sorbent for cobalt(II), copper(II) and cadmium(II) were studied by using the batch method. To obtain adsorption isotherm and determine the adsorption capacity, 50 mL of sample solutions containing 20, 50, 100, 200, 300 and 400 µg L⁻¹ Co(II) and Cd(II) were adjusted to pH 8, and 10, 20, 50 and 100 µg L⁻¹ Cu(II) was adjusted to pH 6 and added to a beaker containing 100 mg of the sorbent. The solutions were shaken for 2 h at 120 rpm at room temperature to reach equilibrium. Then, 10 mL of solution was taken from each solution and amount of residual Co(II), Cu(II) and Cd(II) in the each solution was determined by flame atomic absorption spectrometry.

The profile of adsorption isotherm for Co(II), Cu(II) and Cd(II) were drawn by plotting the milligrams of Co(II), Cu(II) and Cd(II) adsorbed per gram of the sorbent versus the equilibrium concentration of Co(II), Cu(II) and Cd (mg L⁻¹) in solution. By using the data obtained from the adsorption isotherms, the most widely used linearized Langmuir equation [42] given below was obtained. From the slopes and intercepts of the linearized plot of (C_E/Q_E) versus C_E (Figs. 5–7), Langmuir constants (Q₀ and b) were calculated.

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

Table 3

The effect of some foreign ions on the recovery of the Co(II), Cu(II) and Cd(II) ions.

Interfering ions	Concentration (mg L ⁻¹)	Recovery ^a (%)			
		Cd(II)	Cu(II)	Co(II)	
Na ⁺	5	99 ± 2	97 ± 2	99 ± 3	
	25	99 ± 2	95 ± 3	96 ± 2	
	50	95 ± 3	99 ± 4	99 ± 4	
	100	96 ± 3	95 ± 3	88 ± 4	
	250	97 ± 3	90 ± 2	78 ± 3	
	500	82 ± 3	78 ± 4	65 ± 4	
	5	99 ± 2	96 ± 3	94 ± 3	
K ⁺	25	95 ± 3	99 ± 4	98 ± 3	
	50	96 ± 3	100 ± 4	95 ± 4	
	100	95 ± 4	98 ± 2	97 ± 3	
	250	97 ± 4	96 ± 4	95 ± 4	
	500	95 ± 4	95 ± 3	87 ± 3	
	1000	95 ± 2	96 ± 5	73 ± 4	
	1500	81 ± 4	85 ± 3	–	
Ca ²⁺	1	99 ± 3	99 ± 3	97 ± 3	
	5	98 ± 2	98 ± 2	99 ± 2	
	25	97 ± 3	100 ± 4	95 ± 3	
	50	95 ± 4	95 ± 4	95 ± 2	
	100	98 ± 5	98 ± 3	88 ± 4	
	250	60 ± 4	67 ± 5	73 ± 5	
	500	51 ± 4	56 ± 6	54 ± 5	
Mg ²⁺	1	99 ± 2	96 ± 3	99 ± 4	
	5	95 ± 3	98 ± 2	96 ± 3	
	25	96 ± 4	97 ± 3	95 ± 3	
	50	98 ± 3	95 ± 4	90 ± 4	
	100	98 ± 4	98 ± 4	86 ± 5	
	250	98 ± 3	75 ± 5	70 ± 5	
	500	83 ± 2	66 ± 4	56 ± 3	
Zn ²⁺	1	97 ± 3	95 ± 3	98 ± 4	
	5	95 ± 2	99 ± 3	99 ± 3	
	25	95 ± 3	102 ± 3	95 ± 3	
	50	98 ± 5	95 ± 4	86 ± 4	
	100	64 ± 4	86 ± 4	84 ± 4	
	1	99 ± 3	96 ± 4	95 ± 3 (97 ± 2) ^b	
	5	95 ± 4	95 ± 3	88 ± 4 (95 ± 3)	
Ni ²⁺	10	96 ± 3	88 ± 3	76 ± 3 (96 ± 2)	
	25	58 ± 2	75 ± 4	51 ± 4 (95 ± 3)	
	1	99 ± 4	97 ± 3	98 ± 3	
	Fe ³⁺	5	100 ± 3	99 ± 2	95 ± 2
		25	97 ± 4	97 ± 4	94 ± 4
		1	98 ± 2	101 ± 3	–
		5	95 ± 3	98 ± 4	–
Co ²⁺		10	99 ± 4	95 ± 3	–
		25	98 ± 5	97 ± 2	–
		50	85 ± 3	80 ± 5	–
	1	97 ± 3	–	99 ± 4	
	5	95 ± 2	–	102 ± 3	
	Cu ²⁺	25	96 ± 4	–	97 ± 3
		50	95 ± 3	–	95 ± 2
100		87 ± 3	–	88 ± 2	
1		100 ± 3	98 ± 4	99 ± 4	
5		99 ± 4	100 ± 5	101 ± 4	
Mn ²⁺		25	101 ± 4	95 ± 4	85 ± 5
		50	95 ± 3	88 ± 3	82 ± 3
	100	74 ± 5	79 ± 4	71 ± 4	
	1	–	99 ± 4	98 ± 3	
	5	–	95 ± 3	95 ± 4	
	Cd ²⁺	25	–	96 ± 4	86 ± 4
		50	–	90 ± 2	80 ± 2
100		–	75 ± 4	78 ± 4	

^a Mean ± standard deviation for the five determinations.

^b Values in parenthesis are obtained with N₂O-acetylene flame.

where Q₀ (mg g⁻¹) is the maximum amount of the sorbed ions per unit mass of sorbent (capacity parameter) to form a complete monolayer coverage on the surface, C_E (mg L⁻¹) is the equilibrium concentration of analytes, Q_E (mg g⁻¹) is the amount of analyte ions adsorbed per unit mass of sorbent at equilibrium and b (L mg⁻¹) is the Langmuir constant related to the affinity of binding sites and

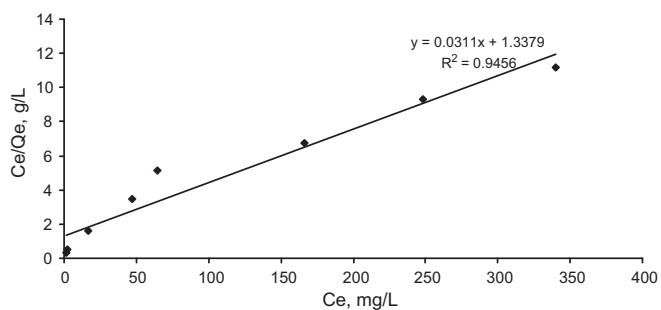


Fig. 5. Linearized Langmuir adsorption isotherm of Co(II) on nano ZrO₂/B₂O₃.

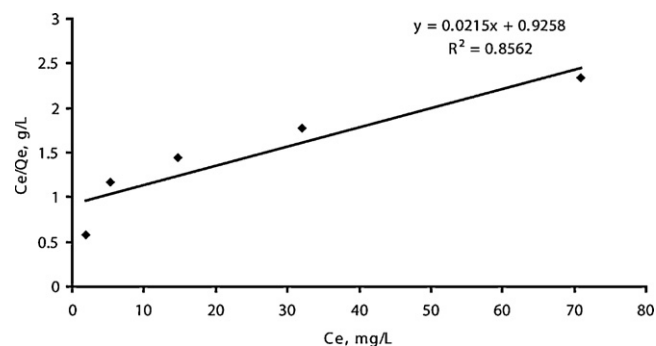


Fig. 6. Linearized Langmuir adsorption isotherm of Cu(II) on nano ZrO₂/B₂O₃.

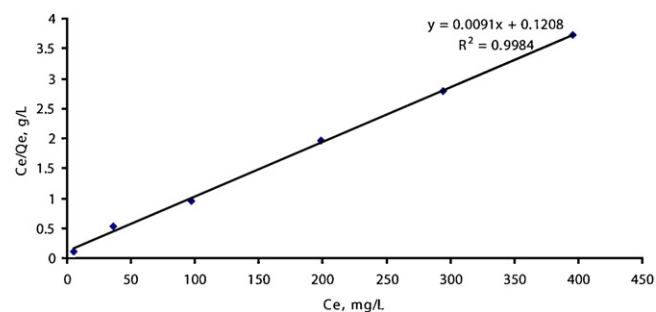


Fig. 7. Linearized Langmuir adsorption isotherm of Cd(II) on nano ZrO₂/B₂O₃.

a measure of the stability of the bond formed between metal ions and adsorbent under specified experimental conditions.

The data of the isotherm reveal that the adsorption process conforms to Langmuir model. The Langmuir adsorption constants calculated from the corresponding isotherms with the correlation coefficients are presented in Table 4. Langmuir adsorption capacities of sorbent for Co(II), Cu(II) and Cd(II) were found as 32.2, 46.5 and 109.9 mg g⁻¹, respectively.

3.9. Analytical figures of merits

As analytical figures of merit, limit of detection (LOD), limit of quantitation (LOQ), precision and accuracy for the proposed method have been investigated. In order to determine the instrumental detection limit for each analyte, 50 mL of blank solution

Table 4
Langmuir constants and correlation coefficients of isotherm models for the sorption of Co(II), Cu(II) and Cd(II) ions from aqueous solutions.

Analytes	Q ₀ (mg g ⁻¹)	b (L mg ⁻¹)	r ²
Cd(II)	109.9	0.075	0.9984
Co(II)	32.2	0.232	0.9456
Cu(II)	46.5	0.023	0.8562

Table 5
Determination of Co(II), Cu(II) and Cd(II) in certified reference material (GBW-07605 Tea leaves).

Analytes	Certified values (μg g ⁻¹)	Found values ^a (μg g ⁻¹)	Relative error (%)	RSD ^b (%)
Cd	0.057 ± 0.008	0.060 ± 0.002	+5.3	3.3
Cu	17.3 ± 0.2	15.6 ± 0.3	-9.8	1.9
Co	0.18 ± 0.02	0.183 ± 0.009	+1.7	4.9

^a Mean of five determinations at 95% confidence level.

^b Relative standard deviation (N = 5).

Table 6
Determination of Co(II), Cu(II) and Cd(II) in tap water.

Analytes	Added (μg mL ⁻¹)	Found ^a (μg mL ⁻¹)	Relative error (%)	RSD ^b (%)
Cd	-	ND ^c	-	-
	1	1.01 ± 0.01	+1	0.99
Cu	-	ND ^c	-	-
	1	1.01 ± 0.01	+1	0.99
Co	-	ND	-	-
	1	0.91 ± 0.03	-9	3.3

^a Mean of five determinations at 95% confidence level.

^b Relative standard deviation (N = 5).

^c Not detected.

was passed through the column under the optimum experimental conditions (pH = 6 for Cu(II) and pH = 8 for Co(II) and Cd(II); eluent, 1.0 mol L⁻¹ HNO₃; flow rate, 5 mL min⁻¹). Blank solutions were prepared by adding a minimum amount of the analytes to the water in order to obtain readable analyte signals. The sorbed analyte was eluted by 50 mL of 1.0 mol L⁻¹ HNO₃ solution (there is no preconcentration) and signal of this blank solution was measured about 20 times. The instrumental detection limits of the elements based on the ratio of three standard deviation of the blank signal to slope of the calibration curve (3 s/b) were found as 38, 33, 46.5 μg L⁻¹ for Co(II), Cu(II) and Cd(II), respectively. The analytical detection limits calculated by dividing the instrumental detection limits [43,44] by the preconcentration factor 15 for Cd(II) and 10 for Co(II) and Cu(II) were 3.8, 3.3, 3.1 μg L⁻¹ for Co(II), Cu(II) and Cd(II), respectively. The analytical limit of quantitation (LOQ) based on 10 s/m were 12.7, 11.0, 10.3 μg L⁻¹ for Co(II), Cu(II) and Cd(II), respectively.

The linear working ranges for the analytes were found as 12.7–5000 μg L⁻¹ for Co(II), 11.0–5000 μg L⁻¹ for Cu(II) and 10.3–3000 μg L⁻¹ for Cd(II) by considering the LOQ values as lower limit of linear working range with a correlation coefficient of about 0.999.

The precision of proposed method evaluated as the standard deviations of recoveries obtained from five replicates under optimum experimental conditions (amount of Co, Cu and Cd, 10 μg; volume of model solution, 50 mL; pH 6.0 for Cu and pH 8.0 for Co and Cd; elution solution, 10 mL, 1.0 mol L⁻¹ HNO₃; flow rate, 5 mL min⁻¹) were 96 ± 3%, 95 ± 3%, 98 ± 4% for Co(II), Cu(II) and Cd(II), respectively.

Table 7
Determination of Co(II), Cu(II) and Cd(II) in tea leaves.

Analytes	Added (μg g ⁻¹)	Found ^a (μg g ⁻¹)	Relative error (%)	RSD ^b (%)
Cd	-	ND ^c	-	-
	5	5.2 ± 0.3	+4	5.8
Cu	-	15.4 ± 0.4	-	2.6
	20	37.8 ± 0.7	+7	1.9
Co	-	ND	-	-
	20	18.8 ± 0.8	-7	4.3

^a Mean of five determinations at 95% confidence level.

^b Relative standard deviation (N = 5).

^c Not detected.

Table 8
Comparative data for various SPE preconcentration methods.

Analytes	Preconcentration system	LOD (ng L ⁻¹)	Adsorption capacity (mg g ⁻¹)	PF	Determination technique ^a	Ref.
V, Cr, Mn, Co, Ni, Cu, Zn, Cd, Pb	Nanometer-sized alumina	6–79	1–18	5	ICP-MS	[19]
Cd	Nano B ₂ O ₃ /TiO ₂	1440	49	100	FAAS	[29]
Cd, Pb	Modified nano alumina	150–170	11.1–16.4	250	FAAS	[31]
Cr, Cu, Pb	Magnetic nanoparticles/bismuthiol II	43–85	5.4–9.4	87–96	FAAS	[32]
Zn, Mn, Ni, Pb, Cd, Cu, Fe, Co	Amberlite XAD-16/DHP	2900–5020	6.7–37.9	200–300	FAAS	[40]
Cu, Co, Cd	Nano ZrO ₂ /B ₂ O ₃	3100–3800	32.2–109.9	10–15	FAAS	This work

^a PF: preconcentration factor; ICP-OES: inductively coupled plasma optical emission spectrometry; ICP-MS: inductively coupled plasma mass spectrometry; FAAS: flame atomic absorption spectrometry.

The accuracy of the proposed method was tested by determining the content of Co(II), Cu(II) and Cd(II) ions in the certified reference materials under optimal experimental conditions. As seen in Table 5, the determined values were in good agreement with the certified values at 95% confidence level. The relative error was found <10% which is acceptable for analytical purposes at these trace metal determinations.

3.10. Application of proposed method

The proposed preconcentration method was applied for determination of Co, Cu and Cd in tap water and tea leaves samples, under optimal experimental conditions. The accuracy of method was also checked by measuring the recovery of Co, Cu and Cd in spiked real samples. A good agreement was obtained between added and found value of the analyte. The results obtained are given in Tables 6 and 7. Relative errors below 10%, demonstrate the applicability of the method and independence from matrix constituents of the samples.

3.11. Comparison of the method with others

The analytical performance of the nanosorbent comparable with the other conventional sorbent or/and nanosorbents. Some comparative data about sorption is summarized in Table 8. Limit of detection, adsorption capacity and preconcentration factors obtained are comparable to those presented by other methods. The present work has relatively high adsorption capacity when compared to other methods [19,29,31,32,40]. Other parameters, limit of detection and preconcentration factor is relatively lower than those of the others methods. However, the proposed method is simpler than the others. For example, there is a no need to use any complexing and/or chelating agent.

4. Conclusion

Nano ZrO₂/B₂O₃ hybrid material as a new solid phase extractor provides a simple, selective, accurate, economical, rapid and precise method for preconcentration and determination of Co, Cu and Cd. There is a no need to use any complexing and/or chelating agent for modifying the sorbent, or for adding to the sample solution to form complex compounds of the analytes before the preconcentration procedure to obtain quantitative recovery of the Pb, Co and Cu. The matrix effect appeared with the use of the proposed method is reasonably tolerable. The adsorbent is stable with a recycling period greater than 100 cycles, without major loss in its quantities and metal recovery property. The enrichment factor, detection limit and adsorption capacity of the new proposed sorbent for Co, Cu

and Cd are also satisfactory. The duration time (time required for passing of sample, elution of analytes and cleaning procedure of the column) is about 1 h for a 250 mL sample solution. The detection limits can be improved by using sensitive method such as ICP-OES and ICP-MS.

Acknowledgement

This work was supported by The Scientific and Technological Research Council of Turkey (TUBITAK, Project No. 106T668).

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