



# Synthesis of nano B<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> composite material as a new solid phase extractor and its application to preconcentration and separation of cadmium

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## ABSTRACT

A new solid phase extractor, nano-scale diboron trioxide/titanium dioxide composite material, was synthesized and used for separation and/or preconcentration of trace cadmium ion from various samples. The characterization of the synthesized material was performed by scanning electron microscope (SEM), transmission electron microscope (TEM) and X-ray diffractometer methods (XRD). The specific surface area of the material was also determined and found as 3.4 m<sup>2</sup>/g. Analytical parameters including pH of sample solution, sample volume, flow rate of sample solution, volume and concentration of eluent for the column solid phase extraction (SPE) procedure were examined. The effect of common matrix ions on the recovery of the cadmium has also been investigated and found that they did not interfere on cadmium preconcentration. Under the optimum experimental conditions, preconcentration factor and analytical detection limit were determined as 50 and 1.44 µg/L, respectively. The reusability (stable up to 100 run) and adsorption capacity (49 mg/g) of the sorbent were excellent. The accuracy of the method was confirmed by analyzing certified reference materials (Tea leaves GBW-07605). The results demonstrated good agreement with the certified values (relative error <10%). The precision of the method was also satisfactory. The recovery of cadmium under the optimum conditions was found to be 96 ± 3% at 95% confidence level. The method was applied for the determination of cadmium in tap water and tea leaves.

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## 1. Introduction

In recent years, determination of ultra trace metals such as cadmium in environmental and food samples has become more serious due to increasingly lower limits imposed on trace metal content of such samples. Cadmium has been described as one of the most dangerous trace metals in the environment of human, not only because of its high level toxicity, but also because of its wide distribution and its many important applications [1]. The FAO/WHO Joint Expert Committee on Food Additives recommended provisional maximum tolerable daily intake of cadmium from all sources (water, food and air) of 1.0–1.2 µg/kg body mass [2]. The maximum permissible level of cadmium in drinking water is 5.0 µg/L [3]. The direct determination of extremely low concentrations of the required trace metals by modern spectroscopic methods is still difficult due to insufficient sensitivity of the techniques and matrix interferences [4]. In order to overcome this problem, preliminary separation and/or preconcentration techniques for the separation of trace metals from complex matrices into a known matrix is widely used [5–7]. Among the preconcentration techniques, solid phase extraction (SPE) has

been used increasingly in compared with other classical methods. Numerous substances have been synthesized and used as solid phase extractor [8–10].

In the past decade, nanometer solid materials have become more and more important due to their special properties [11]. Nanomaterials possess a series of unique physical and chemical properties. One of their important properties is that most of the atoms which have highly chemical activity and adsorption capacities to many metal ions are on the surface of the nanoparticles [12]. The surface atoms are unsaturated, and therefore, are subject to combination with other ions by static electricity [13]. Consequently, nanometer-sized materials can adsorb metal ions with great adsorption speed. Recently nanomaterials have been used as sorbent due to their improved intrinsic properties such as chemical activity and fine grain size in compared with the classical substances such as normal scale titanium dioxide, alumina, etc. [14–16]. Nanomaterials have high surface areas and therefore, they can strongly adsorb many substances such as trace metals [17] and polar organic substances [18]. Nanomaterials can be prepared by various techniques such as chemical vapor deposition [19] and sol–gel method [20,21].

From the literature survey, it can be seen that a lot of different nanomaterials have been synthesized and used as a sorbent for trace metal preconcentration [22–25]. Investigations of the surface chemistry of highly dispersed oxides, e.g., TiO<sub>2</sub> and ZrO<sub>2</sub>, indicate

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that these materials have very high adsorption capacities and give promising results when used for trace metal analyses of different types of solution samples [11,15]. Nano-sized materials were chemically modified by a reagent to obtain a new and selective solid phase extractant for the preconcentration of metal ions [14,15]. Wu et al. described a flow injection method for the determination of Cd(II), Cr(III) and Cu(II) after enrichment on cross-linked chitosan bound FeC nanoparticles and subsequent determination by flame atomic absorption spectrometer (FAAS) [26]. Uheida et al. have been used magnetite nanoparticles coated with nonylthiourea for the separation and recovery of platinum group metals from diluted aqueous chloride solution [27]. Zhai et al. described a rapid, selective method that utilize 4-(2-pyridylazo)-resorcinol (PAR)-modified nanometer SiO<sub>2</sub> as a new solid phase extractor for preconcentration of trace mercury(II) [11]. Deliyanni et al. described batch and column procedure to investigate zinc removal from dilute aqueous solution (i.e., effluent) by sorption onto synthetic nanocrystalline akaganeite, an iron oxyhydroxide [28]. Most of the nanosorbents were used together with either complexing agent or microorganisms to increase the recovery of the analytes [11,15,16,29]. This increases a possible contamination and interferences due to the reagents. This feature also limits the repeated use of sorbent successively. In this study, synthesized nanomaterial could be used without modification with any reagents.

The purpose of this research is to fabricate nano TiO<sub>2</sub>/B<sub>2</sub>O<sub>3</sub> as a new solid phase extractor and to investigate the feasibility of it for using metal enrichment. To the best of our knowledge this is the new solid phase extractor used for this purpose. In this study, synthesized material was first characterized by using scanning electron microscope (SEM), transmission electron microscope (TEM) and X-ray diffractometer methods (XRD) and then used as solid phase extractor for the separation and/or preconcentration of cadmium(II). The procedure was validated by analyzing certified reference materials.

## 2. Experimental

### 2.1. Reagents and solutions

All reagents were of analytical grade, unless otherwise stated. A stock solution of cadmium (1000 mg/L, Merck) was used during the study. Working solutions of the cadmium ion was prepared by suitable dilution of the stock solution. H<sub>3</sub>BO<sub>3</sub> (Carlo Erba, Rodano, Italy), titanium tertbutoxide (Merck, Darmstadt, Germany), ethanol (99.5%, J.T. Baker, Phillipsburg, NJ, USA), Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Carlo Erba), NaNO<sub>3</sub> (Carlo Erba), Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (J.T. Baker), KNO<sub>3</sub> (Merck), MgSO<sub>4</sub> (Carlo Erba), Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Carlo Erba), Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Merck), Pb(NO<sub>3</sub>)<sub>2</sub> (Carlo Erba), HNO<sub>3</sub> (Merck, 65%), HCl (Merck, 37%), NH<sub>3</sub> (Merck, 27%) were used. Ultra pure water (18.3 MΩ cm) was used to prepare all solutions.

### 2.2. Apparatus

The characterization of the synthesized material was performed by scanning electron microscope, transmission electron microscope and X-ray diffractometer methods. A Technai G<sup>2</sup> 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 samples. 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 Nova 2200e (Boynton Beach, Florida, USA) model surface area and pore size analyzer was used for measuring the surface area of material. A

Varian (Palo Alto, CA, USA) AA240FS model flame atomic absorption spectrometer equipped with a deuterium-lamp background corrector, a cadmium hollow cathode lamp (Varian) and an air-acetylene flame as the atomizer was used for the determination of cadmium under the conditions suggested by the manufacturer. The wavelength, lamp current, slit width and acetylene flow rate were 228.8 nm, 4 mA, 0.5 nm and 2.00 L/min, respectively. A Varian AA240Z graphite furnace atomic absorption spectrometer was used for cadmium determination in Certified Reference Material (GBW-07605) using the instrumental parameters recommended by the manufacturer by changing the ash temperature from 250 to 300 °C. All pH measurements were made with a WTW 720 model pH meter (Weilheim, Germany).

### 2.3. Preparation of material

Nano B<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> was synthesized by modifying to the procedure given in literature for synthesizing nano TiO<sub>2</sub> [12]. For this purpose, 3 g of boric acid was added into a flask containing 15 mL ethanol, 10 mL titanium tertbutoxide. The mixture was refluxed at 105 °C, and during the reflux procedure ethanol, water and HCl mixture (12.5 mL + 0.5 mL + 0.25 mL) was added. The mixture was stirred for 3 h at about 100 °C. Then, the mixture was dried for 24 h at 100 °C. The obtained solid material was ground in a ball mill for about 100 min. The powder material was taken in a porcelain crucible and heated at about 450 °C in a furnace and grey colored powder was obtained.

### 2.4. Column preparation

A glass column (150 mm length and 8 mm i.d.) with a glass-wool over its stopcock was used as a mini column. A total of 200 mg of synthesized nano composite material (B<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>) was made slurry in water and then placed into the column. A small amount of glass-wool was placed on top to avoid disturbance the adsorbent during sample passage. The column was preconditioned by passing a blank solution having 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) and water, respectively and stored in water for the next experiment.

### 2.5. Column preconcentration and determination procedure

Proposed preconcentration procedure was tested with model solutions prior to the determination of trace cadmium in samples. An aliquot of a solution (50 mL) containing 5 μg of the cadmium(II) was placed in a beaker and pH of the solution was adjusted to 6 by using diluted HCl or NH<sub>3</sub> solution. The column was preconditioned by passing the aqueous solution of pH 6 through the column and then, the model solution was passed through the column at a flow rate of 2 mL/min. The adsorbed cadmium(II) ions on the column was eluted by using 5 mL of 1 mol/L hydrochloric acid solution. The eluent was analyzed for the determination of cadmium concentration by FAAS. The column has been used repeatedly after washing with 10 mL of 1 mol/L hydrochloric acid solution and ultra pure water, respectively. Using the procedure described above, the recovery of the cadmium was calculated from the ratio of the concentration found by FAAS and the concentration calculated theoretically.

### 2.6. Dissolution of tea leaves (GBW-07605)

Approximately 1.0 g of standard reference material (Tea leaves GBW-07605) was 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

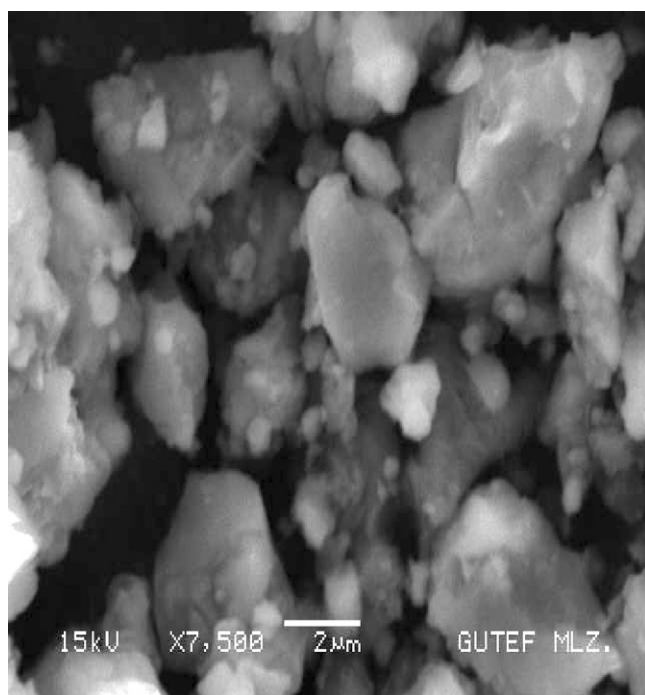


Fig. 1. SEM micrograph of synthesized  $B_2O_3/TiO_2$  nano composite material.

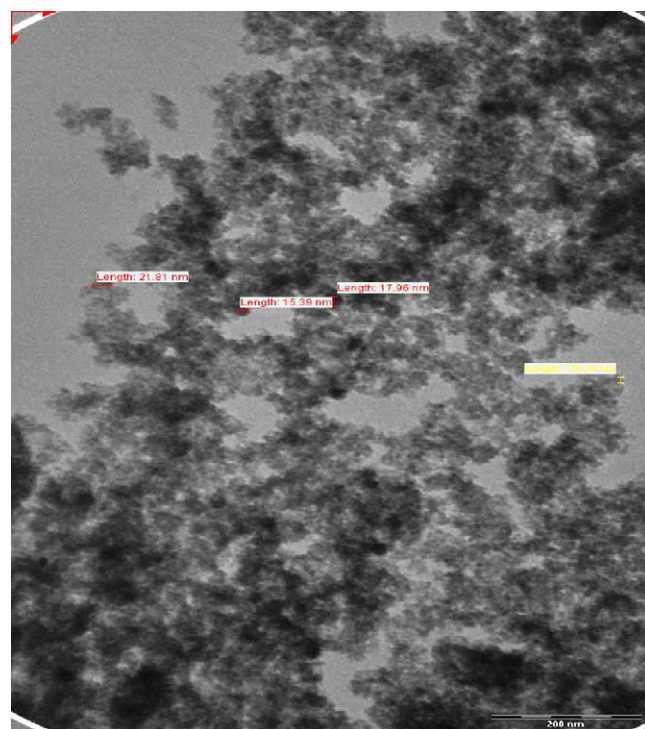


Fig. 2. TEM micrograph of synthesized  $B_2O_3/TiO_2$  nano composite material.

until complete decomposition of the 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.

### 2.7. Preparation of water and tea samples

Tap water sample was collected from the city of Ankara, Turkey and filtered from blue ribbon filter paper before use. Tea sample was purchased from a local market in the city of Ankara, Turkey and 1 g of tea sample was dissolved in 8 mL of concentrated nitric acid and 2 mL of hydrogen peroxide. Sample was decomposed by heating on a hot plate at  $130 \pm 10^\circ C$  and waited for sample evaporation nearly to 2 mL. After decomposing the sample completely, it was transferred to 50 mL volumetric flask by washing interior surface of beakers with  $HNO_3$  (0.5% v/v) three times and diluted to the mark. Sample blank was also prepared by using the procedure given above.

## 3. Results and discussion

### 3.1. Characterization of synthesized material

The synthesized material by the method given above was characterized by scanning electron microscope, transmission electron microscope and X-ray diffraction (XRD) and BET method. Figs. 1 and 2 show SEM and TEM images of nano-scale  $B_2O_3/TiO_2$  composite material. As can be seen from the SEM and TEM images, the  $B_2O_3/TiO_2$  particles are very fine and the grain size is about 15–20 nm levels. From these results, it can be concluded that nano-scale material, which is one of the purpose of the study, could be obtained by the method described above.

In order to characterize the nature of synthesized material, XRD pattern of the material was also investigated. According to the XRD pattern shown in Fig. 3, the nanoparticles are identified as crystalline  $B_2O_3$  and  $TiO_2$ . It can be seen that the synthesized new nanomaterial consisted mainly of  $B_2O_3$  and  $TiO_2$ .

After showing the product was nano-scale  $B_2O_3/TiO_2$ , its specific surface area, which affects the adsorption characteristics of the material, was also investigated. The mean specific surface area of the prepared nanomaterial was estimated to be  $3.4 \text{ m}^2/\text{g}$  (mean of two measurements) by the BET method.

### 3.2. Effect of pH on the adsorption of Cd onto nano $B_2O_3/TiO_2$

The pH value plays an important role to 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 nano-scale  $B_2O_3/TiO_2$  synthesized was studied as a function of pH. For that purpose, the pH values of model sample solutions prepared as given in Section 2.5 were adjusted to a range of 2–10 with HCl or  $NH_3$  solutions keeping the other parameters constant and the general preconcentration procedure was applied. As shown in Fig. 4, the optimum pH of the sample solution was 6 for effective adsorption of cadmium(II). At this pH value, the recovery of the cadmium(II) is above 95%. The decrease in the recoveries of the cadmium(II) at the lower pH values could be due to the competition between protons and the cadmium(II) for the adsorption sites of the sorbent. Therefore, a pH of 6 was selected in further experiments.

### 3.3. Effect of eluent concentration

The type and concentration of eluent is also important for the analytical performance of a column solid phase preconcentration system. Because the adsorption of cadmium(II) is negligible at  $pH < 6$ , various concentrations and various volumes of HCl and  $HNO_3$  were tested for desorption of retained cadmium(II) from the nanosorbent. As a result of the experiments, 5 mL of 1 mol/L HCl solution was found to be satisfactory for cadmium(II) (recovery > 95%) (Table 1).

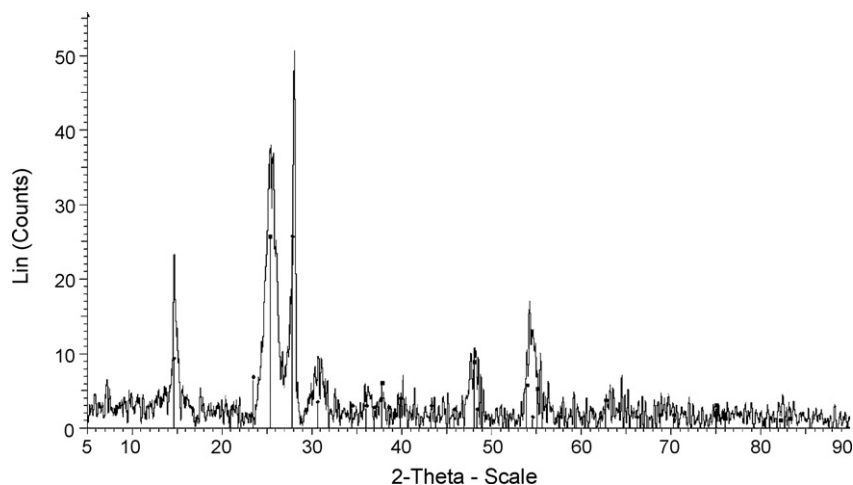


Fig. 3. XRD graph of synthesized  $B_2O_3/TiO_2$  nano composite material.

### 3.4. Effect of flow rate of recovery solution

The retention of element on an adsorbent depends upon the flow rate of sample solution was examined under optimum conditions (pH, eluent type, etc.) by applying the general procedure (Section 2.5). The model cadmium solution (50 mL, 0.1 mg/L Cd(II)) was passed through the column with the flow rates adjusted in a range of 2–4 mL/min. The optimum flow rate was found as 2 mL/min for Cd(II) ion. Therefore, a flow rate of 2 mL/min was selected in further experiments. The flow rate of elution solution was 2 mL/min.

### 3.5. Effect of sample volume

In order to determine the maximum applicable volume of sample solution (or minimum applicable concentration of the cadmium(II)), the effect of the volume of sample solution passed through the column on the retention of cadmium(II), was investigated. For that purpose, 50, 100, 250 and 500 mL of sample solutions containing fixed amount of analyte corresponds to 0.1, 0.05, 0.02 and 0.01  $\mu\text{g/mL}$  of cadmium(II), respectively, were passed

**Table 1**  
The effect of the type and volume of elution solutions on the recovery of Cd(II).

Eluent	Recovery <sup>a</sup> (%)
5 mL of 1 mol/L HCl	100
5 mL of 2 mol/L HCl	105
5 mL of 1 mol/L $HNO_3$	96
5 mL of 2 mol/L $HNO_3$	99

<sup>a</sup> Mean of three replicates.

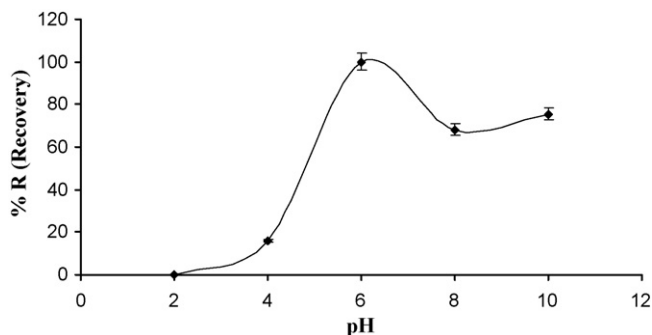


Fig. 4. Effect of pH on the recovery of Cd(II).

through the column under the optimum conditions (pH, flow rate, etc.) determined experimentally. It was found that cadmium(II), up to 250 mL of sample solution could be recovered quantitatively (above 95%). At higher sample volumes, the recoveries decreased gradually with increasing volume of sample solution. Because of the elution volume was 5 mL, a preconcentration factor was obtained 50 for the analyte studied. It can be concluded that 0.02  $\mu\text{g/mL}$  cadmium(II) could be determined by this method for 250 mL of sample volume. However, these concentrations for cadmium(II) cannot be determined directly by FAAS with sufficient accuracy.

### 3.6. 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 ability of regeneration and stability of the column was investigated by passing the analyte and then passing 10 mL of 1 mol/L HCl and 50 mL of ultra pure water through the column packed with 200 mg of  $B_2O_3/TiO_2$  nano composite. The adsorbent was always stored in water. It was observed that the column could be reused up to 100 runs without a decrease in the recoveries of cadmium(II). The number of adsorption–desorption cycles of the proposed nanosorbent is significantly higher than the conventional sorbents previously reported in the literature [8,30].

### 3.7. Adsorption isotherm and adsorption capacity

The adsorption capacity is an important factor to evaluate the property of sorbent, because it determines how much sorbent is required to quantitatively concentrate the analytes from a given solution. To determine the adsorption capacity, 50 mL of sample solutions containing 20, 50, 100, 200, 300, 400 and 500  $\mu\text{g/mL}$  cadmium(II) were adjusted to pH 6 and batch procedure was applied by using 100 mg of  $B_2O_3/TiO_2$  nanomaterial. The solutions were shaken for 2 h at 120 rpm at room temperature. Then, 10 mL of solution was taken from each solution and the amount of residual cadmium(II) in the solution was determined by flame atomic absorption spectrometry. The profile of the adsorption isotherm for cadmium(II) was drawn by plotting the equilibrium concentration of cadmium(II) (mg/L) versus the milligrams of cadmium(II) adsorbed per gram  $B_2O_3/TiO_2$  nano composite, and shown in Fig. 5.

The data of the isotherm reveal that the adsorption process conforms to the Langmuir model. In Fig. 5, the graph shows an excellent

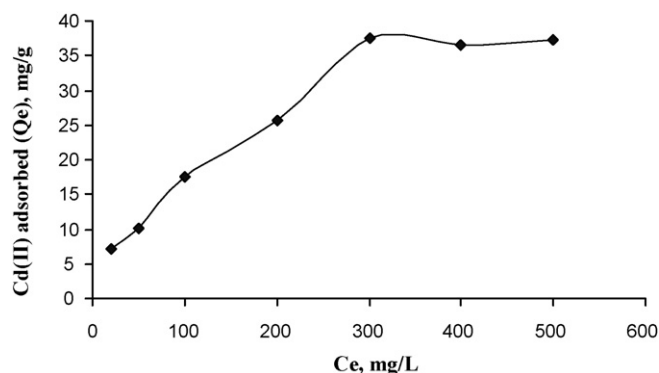


Fig. 5. Adsorption isotherm of  $B_2O_3/TiO_2$  nano composite material for cadmium(II) in batch procedure.

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 Cd(II) in the solution at equilibrium (mg/L),  $Q_E$  is the amount of sorbed cadmium per gram of resin at equilibrium (mg/g),  $b$  is the “affinity” parameter or Langmuir constant (L/mg) and  $Q_0$  is the “capacity” parameter (mg/g). Based on the linearized form of the adsorption isotherm derived from plots of  $C_E/Q_E$  versus  $C_E$ , the constant  $Q_0$  values were calculated from the slope of the graph (Fig. 6). The value of  $Q_0$  is found to be 49 mg/g. The Langmuir constant is 0.007 L/mg.

### 3.8. Effect of foreign ions

In order to demonstrate the applicability of the method, the effect of common matrix ions which may interfere with the determination of cadmium(II) was examined. Interferences from alkali metal ions [Na(I) and K(I)], alkaline earth metal ions [Ca(II) and Mg(II)] which are found generally in high concentration in water samples and some trace elements, Ni, Al, Pb and Co, on the preconcentration of cadmium(II) was investigated. In these experiments, solutions of 0.1 ng/mL of cadmium(II) containing the added interfering ions were treated according to the recommended procedure. There was no obvious influence on the recovery of cadmium(II) for Na, K and Mg up to 5000  $\mu\text{g/mL}$ , for Ca and Ni up to 500  $\mu\text{g/mL}$  and for Al and Co up to 50  $\mu\text{g/mL}$ . The results are summarized in Table 2. As it can be seen, matrix ions studied have no considerable effect on the determination of cadmium(II).

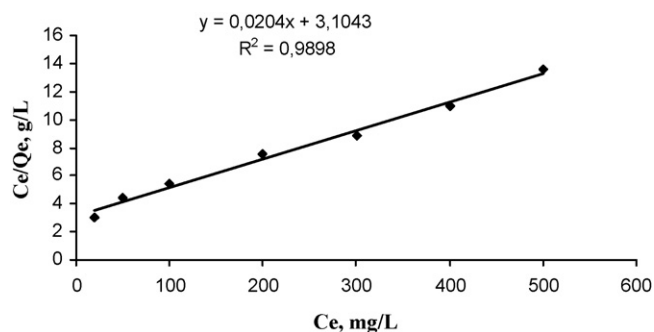


Fig. 6. Linearized Langmuir isotherm obtained from the cadmium(II) adsorption on  $B_2O_3/TiO_2$  nano composite.

Table 2

Effect of other ions on the recovery of Cd(II) (concentration of Cd(II), 0.1  $\mu\text{g/mL}$ ; sample volume, 50 mL).

Interfering ions	Concentration (Hg/mL)	Recovery (R%) <sup>a</sup>
–	–	96 ± 3
Na <sup>+</sup>	5	99 ± 2
	50	99 ± 2
	500	99 ± 3
	5000	99 ± 3
	–	–
K <sup>+</sup>	5	99 ± 2
	50	99 ± 3
	500	99 ± 3
	5000	99 ± 4
	–	–
Ca <sup>2+</sup>	5	99 ± 2
	50	99 ± 2
	500	99 ± 3
	2500	99 ± 3
	5000	70 ± 4
Mg <sup>2+</sup>	5	99 ± 2
	50	99 ± 3
	500	99 ± 4
	5000	99 ± 3
	–	–
Al <sup>3+</sup>	5	98 ± 2
	50	87 ± 3
Ni <sup>2+</sup>	5	99 ± 3
	50	99 ± 3
	500	99 ± 2
	5000	87 ± 4
Co <sup>2+</sup>	5	98 ± 2
	50	65 ± 3

<sup>a</sup> Mean of three determinations ± standard deviation.

### 3.9. Analytical features

In order to determine the instrumental detection limit, 50 mL of blank solution was adjusted to pH 6 and then, this solution was passed through the column. Blank solution was prepared by adding a minimum amount of cadmium to the water in order to obtain readable cadmium signal. The column was washed by 50 mL of 1 mol/L hydrochloric acid solution (there is no preconcentration). The instrumental detection limit based on mean of blank values plus three times the standard deviation of the blank values was found to be 72  $\mu\text{g/L}$  for cadmium ( $N=20$ ). The analytical detection limit calculated by dividing the instrumental detection limit by the preconcentration factor (50) was 1.44  $\mu\text{g/L}$  [31]. The limit of quantification (LOQ) is accepted that it usually equals about three times the LOD value. Therefore, LOQ values of Cd(II) is 4.32  $\mu\text{g/L}$ .

The calibration graph was linear with a correlation coefficient of about 0.999 up to 3  $\mu\text{g/mL}$  Cd(II) from LOQ value of 216  $\mu\text{g/L}$  ( $72 \times 3$ ) by applying direct aspiration without the preconcentration step.

The time required for preconcentration of 100 mL of sample solution (50 min, at flow rate of 2 mL/min), elution (5 min, at flow rate of 2 mL/min) and conditioning the column (about 5 min) was approximately 60 min.

Table 3

Determination of cadmium(II) in various samples (volume of tap water sample, 250 mL; amount of tea, 1.0 g).

Sample	Added	Found <sup>a</sup> $\bar{x} \pm (ts/\sqrt{N})$	Recovery (%)
Tea	–	0.36 ± 0.17 $\mu\text{g/g}$	–
	5 $\mu\text{g/g}$	5.81 ± 0.52 $\mu\text{g/g}$	108
Tap water	–	ND <sup>b</sup>	–
	1 $\mu\text{g/mL}$	1.01 ± 0.01 $\mu\text{g/mL}$	101

<sup>a</sup> Mean of five determinations at 95% confidence level.

<sup>b</sup> ND: Not detected.

**Table 4**  
Comparative data on various sorbents for cadmium(II) preconcentration.

Sample	Preconcentration technique	Determination technique	PF <sup>a</sup>	LOD <sup>a</sup>	Reusability (cycles) <sup>a</sup>	Ref.
Lake water	Nanometer-size titanium dioxide immobilized silica gel, column technique	ICP-OES	50	48 ng/L	20	[12]
Tobacco	2-Aminothiophenol functionalized amberlite XAD-4, column technique (online preconcentration)	FAAS	99	0.3 µg/L	–	[32]
Water	4-(8-Hydroxy-5-quinolylazo)naphthalenesulfonic acid modified silica gel, batch and column technique	ICP-OES	50	2.2 ng/mL	–	[33]
Water	Nanometer-sized alumina coated with chromotropic acid, column technique	ICP-OES	50	0.14 µg/L	15	[34]
Water	Nanometer-sized alumina, column technique	ICP-MS	5	0.079 µg/L	50	[35]
Water	Nanometer-size titanium dioxide, batch technique	FAAS	12.5	3.0 µg/L	–	[36]
Tap water, tea	Nanometer-size boron oxide/titanium dioxide composite, column technique	FAAS	50	1.44 µg/L	100	This work

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

<sup>a</sup> Data were given only for Cd(II).

In order to determine the precision of the method, the proposed method was applied successively by using the model solutions containing 0.1 µg/mL cadmium(II) under the optimum conditions. The cadmium(II) concentration in elution solution was determined by FAAS. The mean recoveries for seven determinations at 95% confidence level were  $96 \pm 3\%$  for Cd(II). The percent relative standard deviation of recoveries was  $\leq 3.0\%$ .

In order to evaluate the accuracy of the developed procedure, cadmium was determined in the certified reference material [The composition of the tea leaves powder (GBW-07605) is Fe 264, Ni 4.6, Cu 17.3, Pb 4.4, Zn 26.3, Cd 0.057, Cr 0.80, Co 0.18, Sb 0.056 and Bi 0.063 (µg/g)]. Cadmium concentration found as the mean of five determinations at 95% confidence level was  $0.062 \pm 0.001$  µg/g with a relative error of % 8.8. It was found that there is no significant difference between result found by the proposed method and certified value ( $0.057 \pm 0.008$  µg/g) according to the *t*-test. It can be concluded that there is no systematic error in the determination at 95% confidence level.

### 3.10. Application of the proposed method

Since it was found that the proposed preconcentration method was useful for the preconcentration of trace cadmium in the presence of other metal ions, in order to show the applicability of the method, the proposed method was applied to the determination of cadmium in tap water and tea leaves under optimal experimental conditions (pH, 6; flow rate, 2 mL/min; eluent, 5 mL of 1 mol/L HCl). The accuracy of the method was also checked by measuring the recovery of cadmium(II) in spiked real samples. A good agreement was obtained between added and found value of the analyte. The results obtained are given in Table 3. Relative errors, below 10%, demonstrate the applicability of the method and independence from matrix constituents of the samples.

## 4. Conclusion

Nano B<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> composite material as a new solid phase extractor provides a simple, selective, accurate, economical, rapid and precise method for the preconcentration and determination of cadmium. There is no need for loading of any chelating and/or complexing agent or microorganism onto the sorbent before the preconcentration procedure to obtain quantitative recovery of cadmium ion. This minimizes a possible contamination and interferences due to the reagents. This feature also allows repeated use of sorbent. It was found that the recovery values of the cadmium after 100 cycles of adsorption and desorption were still quantitative. Another advantage of the method is permitting to study in acidic medium that minimize precipitation of metal hydroxides.

The enrichment factor, detection limit and the adsorption capacity of this new nanosorbent for cadmium are also satisfactory. The detection limit can be improved by using more sensitive detectors such as ICP-AES and ICP-MS. The analytical performance of the nanosorbent is comparable with the other conventional sorbents and/or nanosorbents. Some comparative data about sorption are summarized in Table 4. The proposed technique can be successfully applied to environmental samples for the determination of traces of the cadmium(II). The main disadvantage of the proposed method is the duration time of the preconcentration step. The duration time is about 5 h for a 500 mL of sample solution.

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