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## Synthesis of nanocrystalline $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for solid phase extraction of cadmium and flame atomic absorption determination

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### ABSTRACT

In this paper, mesoporous nanocrystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with high surface area was synthesized with a facile synthesis method and employed as column sorbent for extracting trace amount of cadmium. The synthesized  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> showed high surface area (491 m<sup>2</sup> g<sup>-1</sup>) with a particle size of around 3 nm. The effect of various parameters such as pH, sample flow rate, type and amount of solvent, and the effect of foreign ions were investigated. For this purpose, a sample volume containing a small amount of cadmium with pH = 7-7.5 was passed through a microcolumn packed with nanocrystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and the retained cadmium was washed with 2.0 mL of nitric acid (0.5 mol L<sup>-1</sup>) and determined with flame atomic absorption spectrometry. The dynamic linear range of method was between 1.0-15.0 and the detection limit of method was 0.16  $\mu$ g L<sup>-1</sup>. This method has been successfully used for evaluating and measuring of cadmium in the real samples.

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### KEYWORDS

Nanocrystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>;  
Preconcentration;  
Cadmium;  
Water samples.

### INTRODUCTION

Cadmium is from one of the elements that not only don't play being in the human body, but also, is now known to be extremely toxic. This element and solution of its combinations are poisonous and they are stored in organs of the body and environment. Inhaling cadmium causes some problems in kidneys and can also causes death. Environmental exposure to cadmium has been particularly problematic in Japan where many people have consumed rice grown in cadmium contaminated irrigation water. This phenomenon is known

under the name itai-itai disease<sup>[1]</sup>. Nickel-cadmium batteries are one of the most popular and most common cadmium-based products. These industrial activities cause the cadmium release into the aquatic environment. Environmental pollution of natural waters by toxic inorganic cadmium arises mainly from industrial effluents and wastewater disposal from different sources, such as nickel-cadmium batteries, pigments, chemical stabilizers, alloys and fertilizers. Its presence in abnormally high levels can cause a series of adverse reactions<sup>[2-4]</sup>. All these facts, which cause alarm in the public health, demand accurate analytical procedures for the

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quantification of this element at, trace levels. Based on American Environmental Protection Agency (U.S. EPA) standards a maximum contaminant level of cadmium equal to 10 mg L<sup>-1</sup> in drinking water is allowed. The official regulations have shown a worldwide tendency to lower the maximum permissible levels of cadmium.

Since the content of cadmium ions in natural water and drinking water is commonly at a very low level, the detection limit for cadmium cannot meet the requirement by modern atomic spectroscopic methods such as flame atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES). The analysis of low concentration level requires the introduction of a preconcentration step previous to instrumental detection. Nowadays, various technologies and methods have been developed for the analysis of cadmium ions at trace levels, including solid-phase extraction and flame atomic absorption spectrometry<sup>[5-7]</sup>, cloud point extraction and flame atomic absorption spectrometric determination<sup>[8-10]</sup>, voltammetry<sup>[11]</sup>, supported liquid membrane extraction atomic absorption spectrophotometer determination<sup>[12]</sup>, and liquid-liquid microextraction combined with electrothermal atomic absorption spectrometry<sup>[13,14]</sup>.

Solid-phase extraction of traces of heavy metal ions is widely used in preconcentration methodology. Batch and column procedures are the two important parts of the solid-phase extraction. Recently nanomaterials have been used as sorbent in solid phase extraction due to their improved intrinsic properties such as chemical activity and fine grain size in compared with the classical substances. Nanometer solid materials as a new material category have become more and more important due to their special properties in recent years. Nanomaterials possess a series of unique physical and chemical properties and can adsorb metal ions with high capacities on surface of themselves<sup>[15,16]</sup>. One of nanoparticles' properties is that most of the atoms are on the surface. Investigations of the surface chemistry of highly dispersed oxides indicate that these materials have a very high adsorptive capacity and give promising results when used for trace-metal analyses of different types of water and solutions. Nanometer-sized alumina is resistant to pH changes and has a strong resistance to swelling when placed in organic solvents. Moreover, the preparation of this material is very simple

and beneficial when compared with other commercially available solid phase materials. Nanometer-sized alumina has high surface area, high adsorption capacity and high chemical activity and thus it could be successfully applied for the separation and determination of trace metal ions in environmental samples.

In this work, we studied the adsorption behavior of cadmium ions on mesoporous nanocrystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with high surface area as the preconcentration step for determination of cadmium in aqueous samples. The adsorption behaviour of nanocrystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and the optimum conditions for the preconcentration were investigated and the developed method was applied to the determination of cadmium ions in the drinking and river water sample successfully.

## EXPERIMENTAL

### Reagents

Aluminium i-propoxide and sucrose, nitric acid, hydrochloric acid, and sulfuric acid were purchased from Merck (Darmstadt, Germany) and used without further purification. Cadmium standard solution (1000 mg L<sup>-1</sup>) and ICP multi element standard were obtained from Merck (Darmstadt, Germany). The working Cd<sup>2+</sup> standard solutions were prepared by dilution of cadmium standard solution in water. Ultrapure water was prepared by a Direct-Q 3 UV system (Millipore, Molsheim, France).

### Apparatus

The cadmium determination was carried out on a 20 plus Varian atomic absorption spectrometer with a hollow cathode lamp at a wavelength of 228.8 nm and a slit of 0.5 nm using an air/acetylene flame. Oil-less vacuum pump (Rocker 600, Today's, Taiwan) was used for passing the solution. The pH value was measured with a Metrohm pH meter (model 827) equipped with a combined glass-calomel electrode. Porosity and surface area studies were performed on a Micrometrics Tristar 3000 automated gas adsorption system. All the samples were out gassed at 350°C under vacuum prior to N<sub>2</sub> adsorption at -196°C. Surface areas were calculated according to the BET equation, while pore size distributions were derived from the desorption isotherm using the BJH model. Transmission electron micros-

copy (TEM) studies were performed using a JEOL 4000EX microscope operated at 300 kV.

### Preparation of alumina

The mesoporous nanocrystalline  $\gamma$ - $\text{Al}_2\text{O}_3$  with high surface area was prepared using the following procedure: 4.2 g of aluminium *i*-propoxide and 7.2 g of sucrose were dissolved in 36 mL of distilled water; the resultant solution was stirred at room temperature for 30 min. Afterwards a diluted aqueous nitric acid solution (10 % wt) was added drop-wise to adjust the pH value. After 5 hours, the mixture was heated at 100°C in air atmosphere to remove water and all other volatiles. The resulted solid was then calcinated at 600 °C for 6 h to remove the template.

### Column preparation for solid phase extraction

A glass column (50 mm length and 8mm i.d.) with a frit filter was used as column. A total of 100 mg of synthesized nanocrystalline  $\gamma$ - $\text{Al}_2\text{O}_3$  was made slurry in water and then placed into the column. A frit filter was placed on top to avoid disturbance the adsorbent during sample passage.

## RESULTS AND DISCUSSION

### Characterization of nanometer sized $\gamma$ - $\text{Al}_2\text{O}_3$

The purity of the prepared  $\gamma$ - $\text{Al}_2\text{O}_3$  nanoparticles was examined using X-ray diffraction. The XRD pattern of the final powders is shown in Figure 1, which clearly indicates that the sample is in the gamma phase in nature. Figure 2 shows the pore size distributions and  $\text{N}_2$  adsorption/desorption isotherms for the samples prepared under different pH values. It is seen that all samples are mesoporous and show almost the same pore size distribution. All the samples show a narrow pore size distribution. It seems that the sample prepared under pH value of 5 shows a narrower pore size distribution than those obtained for other samples. The nitrogen adsorption/desorption isotherms (Upper inset) can be classified as a type IV isotherm, typical of mesoporous materials. According to IUPAC classification, the hysteresis loop is a type  $\text{H}_2$  indicating a complex mesoporous structure. The appearance of type  $\text{H}_2$  hysteresis loops in the isotherms indicated the presence of “ink-bottle” type pores in the prepared samples. The specific sur-

face area of mesoporous alumina prepared using this method can be up to 491  $\text{m}^2 \text{g}^{-1}$ . The obtained results also showed that the specific surface area and the pore size can be tuned by changing the pH value of the starting solution (TABLE 1).

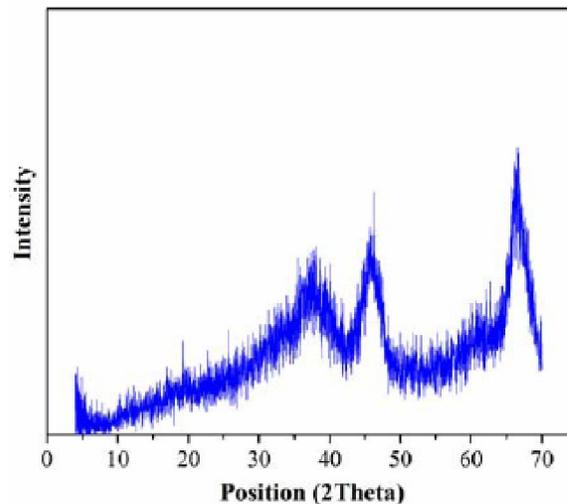


Figure 1 : XRD patterns of synthesized mesoporous nanocrystalline  $\gamma$ - $\text{Al}_2\text{O}_3$  prepared at pH of 5.

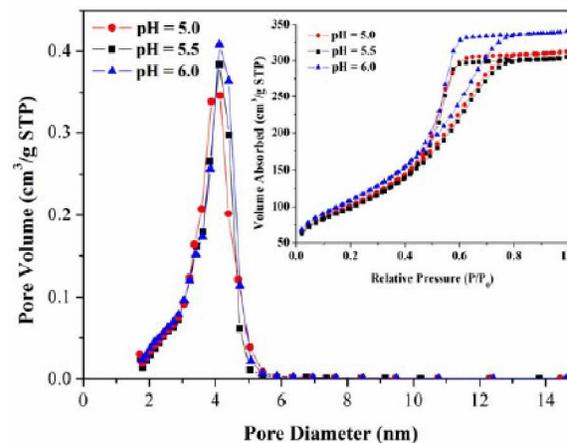


Figure 2 : Pore size distributions and  $\text{N}_2$  adsorption/desorption isotherms (upper inset) obtained for synthesized mesoporous nanocrystalline  $\gamma$ - $\text{Al}_2\text{O}_3$ .

TABLE 1 : Structural properties of the synthesized mesoporous nanocrystalline  $\gamma$ - $\text{Al}_2\text{O}_3$ .

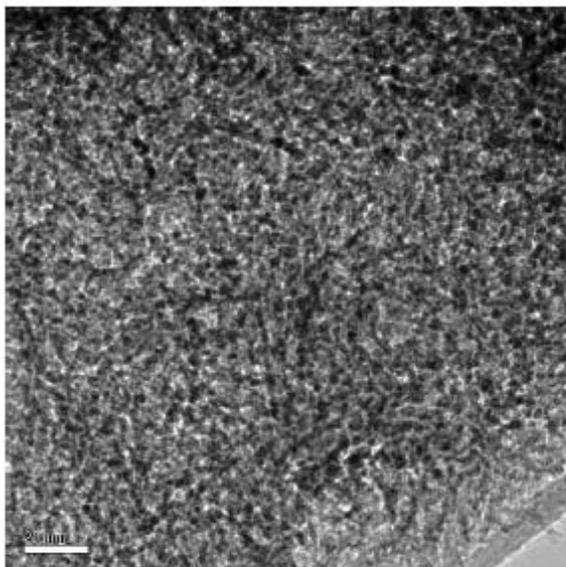
pH	BET area ( $\text{m}^2 \text{g}^{-1}$ )	Pore volume ( $\text{cm}^3 \text{g}^{-1}$ )	Pore diameter (nm)	Particle size (nm)
5.0	441	0.60	4.1	3.7
5.5	491	0.62	4.2	3.3
6.0	464	0.63	4.4	3.5

The theoretical particle sizes were also calculated from surface area, assuming spherical particles, from the following equation:

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$$D_{\text{BET}} = \frac{6000}{\rho \times S} \quad (1)$$

Where  $D_{\text{BET}}$  the equivalent particle diameter in nanometers is,  $\rho$  is the density of the material in  $\text{g cm}^{-3}$  and  $S$  is the specific surface area in  $\text{m}^2 \text{g}^{-1}$ . The obtained results showed a particle size ranged between 3.3-3.7 nm. Transmission electron microscopy (TEM) image (Figure 3) of mesoporous alumina prepared by sucrose templating (pH: 5.5) showed a nanostructure with a wormhole-like appearance and no significant order of pore arrangement.



**Figure 3 :** TEM image of synthesized mesoporous nanocrystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> prepared under pH value of 5.5 after calcination at 600°C.

### Solid phase extraction procedure

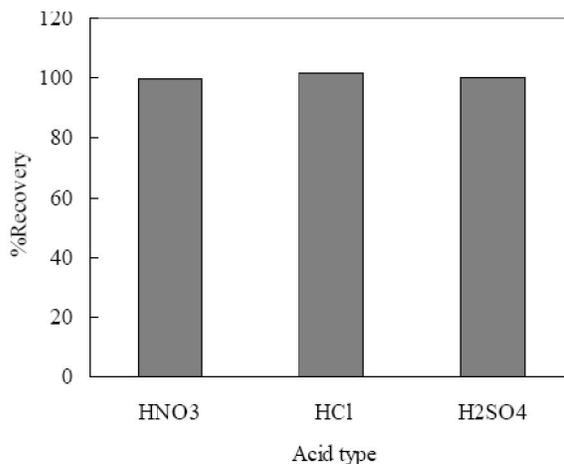
The column was preconditioned by passing a blank solution having same pH with the sample solution prior to use. After each use, the nanomaterial in the column was washed with 5 mL dilute HNO<sub>3</sub> (1.0 mol L<sup>-1</sup>) and water, respectively and stored in water for the next experiment. An aliquot of solution containing 6.0  $\mu\text{g L}^{-1}$  of cadmium adjusted at appropriate pH with ammonium acetate/acetic acid buffer was passed through the column at a flow rate of 10 mL min<sup>-1</sup> using a vacuum pump. After passing the solution the retained metal ions were eluted from the column by acidic solution and the concentrations of metal ions were determined by FAAS.

In order to get the best performance for the solid phase extraction, the effect of various variables on the

preconcentration and determination of cadmium were studied and optimized using the one-at-a-time optimization method.

### Eluent selection

It was an important step to quantitatively recover the retained analytes from the sorbent in the SPE procedure. A suitable eluent composed of 0.5 N HNO<sub>3</sub>, HCl and H<sub>2</sub>SO<sub>4</sub> were used. Because of this purpose about 100 mL solution of 6.0  $\mu\text{g L}^{-1}$  of Cd<sup>2+</sup> containing 0.1 mol L<sup>-1</sup> of ammonium acetate/acetic acid with (pH~7) was passed through alumina cartridge and eluted with 5.0 mL of 0.5 mol L<sup>-1</sup> HNO<sub>3</sub>, HCl and 0.25 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> separately and the solution was used for Cd<sup>2+</sup> measurement. The obtained results showed that the average of the desorption of Cd<sup>2+</sup> for all acids is about 100 percent (Figure 4), but due to the fact that nitrate was a more acceptable matrix for both flame atomic absorption spectrometry experiments than other anions, the nitric acid was selected as elution solvent.

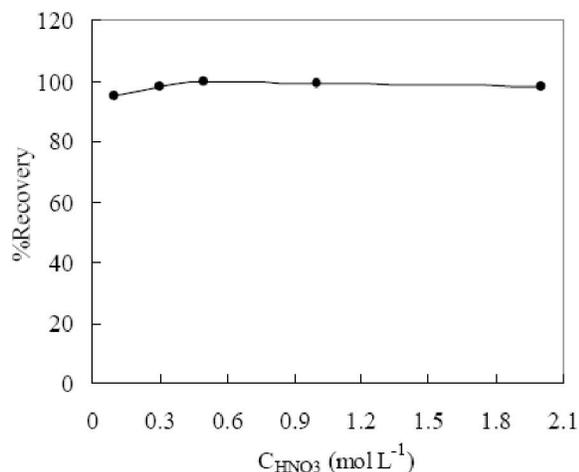


**Figure 4 :** Effect of acid type on recovery on cadmium ions from nano-alumina. Volume of sample: 100 mL; volume of eluent: 5 mL, concentration of eluent: 0.5 mol L<sup>-1</sup>; flow rate of sample solution 10 mL min<sup>-1</sup>; flow rate of eluent: 5 mL min<sup>-1</sup>; pH = 7.0; cadmium concentration 6.0  $\mu\text{g L}^{-1}$ .

### Concentration and volume of eluent

To investigate the effect of concentration and volume of eluent, 100 mL of the 6.0  $\mu\text{g L}^{-1}$  solution of Cd<sup>2+</sup> organized with ammonium acetate/acetic acid (0.1 mol L<sup>-1</sup>) was passed through the alumina cartridge and washed with 5.0 mL of HNO<sub>3</sub> with different concentrations ranged between 0.1-2 mol L<sup>-1</sup> and the solution used for measuring of Cd<sup>2+</sup>. Results showed that from

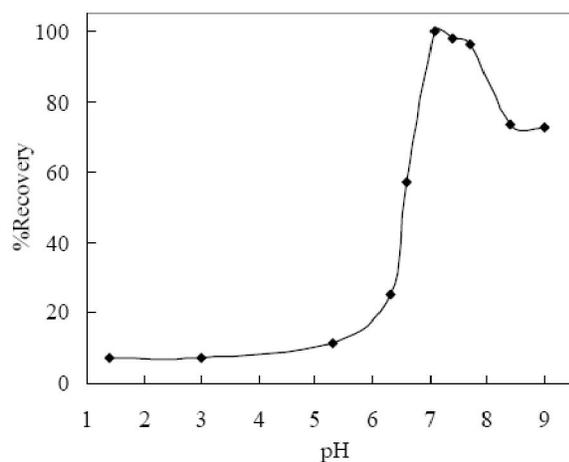
concentration of  $0.3 \text{ mol L}^{-1}$ ,  $\text{Cd}^{2+}$  ions will be washed from the surface of the alumina quantitatively (Figure 5). Thus,  $0.5 \text{ mol L}^{-1} \text{HNO}_3$  was selected for subsequent experiments. The quantitative stripping of the retained  $\text{Cd}^{2+}$  ions by the cartridge was then studied by using various volumes (1.0-8.0 mL) of  $0.5 \text{ mol L}^{-1} \text{HNO}_3$ , and it was found and that at least 2.0 mL of  $0.5 \text{ mol L}^{-1} \text{HNO}_3$  is required for this purpose (Data was not shown).



**Figure 5 :** Effect of  $\text{HNO}_3$  concentration on desorption of cadmium ions from nano-alumina, volume of sample: 100 mL; volume of eluent: 5 mL; flow rate of sample solution  $10 \text{ mL min}^{-1}$  flow rate of eluent:  $5 \text{ mL min}^{-1}$ ; pH = 7.0; cadmium concentration  $6.0 \mu\text{g L}^{-1}$ .

### Effect of pH

To investigate the effect of pH, different solutions



**Figure 6 :** Effect of pH of sample solution on adsorption of cadmium ions by nano-alumina. Volume of sample: 100 mL; volume of eluent; concentration of eluent:  $0.5 \text{ mol L}^{-1}$ ; 2.0 mL; flow rate of sample solution  $10 \text{ mL min}^{-1}$ ; flow rate of eluent:  $5 \text{ mL min}^{-1}$ ; cadmium concentration  $6.0 \mu\text{g L}^{-1}$ .

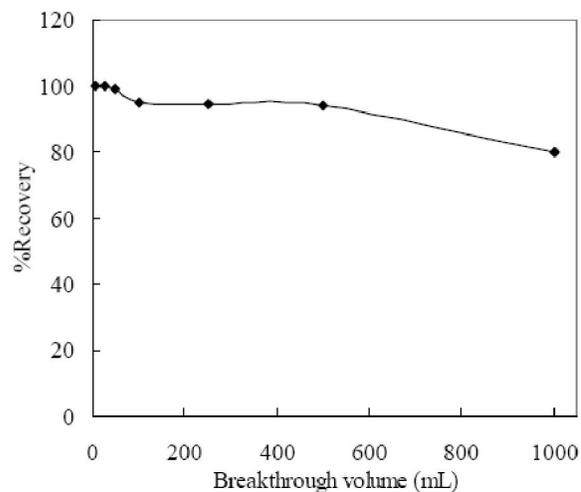
(100 mL) with a  $\text{Cd}^{2+}$  concentration of  $6.0 \mu\text{g L}^{-1}$  with different adjusted pH ranged between 1.4-9 were prepared and passed through the packed column, separately. The pH was adjusted using ammonium acetate/acetic acid, NaOH and  $\text{HNO}_3$  ( $0.1 \text{ mol L}^{-1}$ ). The result obtained showed that in pH 7.0-7.5 of  $\text{Cd}^{2+}$  ions were retained completely by sorbent (Figure 6).

### Effect of solution and eluent flow rate

To determine the effect of flow rate on retention of cadmium ions on the surface of alumina cartridge, different sample flow rates ranged between  $5\text{-}25 \text{ mL min}^{-1}$  were examined. The results showed that the sample flow rate in the studied range didn't have any effect on retention of cadmium ions on the surface of the cartridge. Subsequent experiments showed that the flow rate of eluent have any influences on extraction (Data was not shown).

### Effect of breakthrough volume

In order to determine the effect of sample volume on the  $\text{Cd}^{2+}$  extraction, 0.5 mL of solution containing  $1.0 \text{ mg L}^{-1}$  of  $\text{Cd}^{2+}$  was poured separately into 50, 100, 250, 500 and 1000 mL volumetric flasks and diluted with ultrapure water to prepare solutions with concentrations of 10.0, 5.0, 2.0,  $1.0 \mu\text{g L}^{-1}$ , respectively. These solutions were passed through the alumina cartridge according to general procedure described in sample preparation section. The obtained



**Figure 7 :** Effect of volume of sample on adsorption of cadmium ions by nano-alumina. volume of eluent, 2.0 mL; concentration of eluent:  $0.5 \text{ mol L}^{-1}$ ; 2.0 mL; flow rate of sample solution  $10 \text{ mL min}^{-1}$ ; flow rate of eluent:  $5 \text{ mL min}^{-1}$ ; pH = 7.3; cadmium concentration  $6.0 \mu\text{g L}^{-1}$ .

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results showed that in the range of 50-500 mL of sample volume the extraction efficiency is nearly quantitative and for sample volume of 1000 mL the recovery is 80% (Figure 7). This means that for real examples we can pass sample volumes up to 500 mL through the cartridge and after elution with 2.0 mL of eluent (HNO<sub>3</sub>), one can obtain preconcentration factor of 250.

### The effect of foreign ions

To investigate the effect of other ions on Cd<sup>2+</sup> extraction, 250 mL of solution containing 6.0  $\mu\text{g L}^{-1}$  of Cd<sup>2+</sup> at pH =7.1 passed through the cartridge in the presence of other ions. After washing the cartridge with 2.0 mL of 0.5 mol L<sup>-1</sup> HNO<sub>3</sub>, the obtained solution was analysed. Results showed that bothering ions have any influences on extraction and desorption of the Cd<sup>2+</sup> from the surface of the cartridge (TABLE 2).

TABLE 2 : Effect of foreign ion on recovery of cadmium ion.

Foreign ion	Ratio of foreign ion to Cd <sup>2+</sup> ion (w/w)	Recovery %	Foreign ion	Ratio of foreign ion to Cd <sup>2+</sup> ion (w/w)	Recovery %
Ag <sup>+</sup>	100	99	In <sup>3+</sup>	100	100
Al <sup>3+</sup>	100	98	K <sup>+</sup>	100	102
B <sup>3+</sup>	100	100	Li <sup>+</sup>	100	103
Ba <sup>2+</sup>	100	98	Mg <sup>2+</sup>	100	100
Bi <sup>3+</sup>	100	100	Mn <sup>2+</sup>	100	98
Ca <sup>2+</sup>	100	101	Na <sup>+</sup>	100	99
Co <sup>2+</sup>	100	97	Ni <sup>2+</sup>	100	97
Cr <sup>6+</sup>	100	98	Pb <sup>2+</sup>	100	98
Cu <sup>2+</sup>	100	100	Sr <sup>2+</sup>	100	101
Fe <sup>3+</sup>	100	95	Tl <sup>+</sup>	100	102
Ga <sup>3+</sup>	100	100	Zn <sup>2+</sup>	100	101

### Analytical performances

Calibration curve was obtained after extraction of 500 mL of sample solution containing cadmium ions ranged between 1.0–15.0  $\mu\text{g L}^{-1}$  and elution with 2.0 mL of HNO<sub>3</sub> 0.5 mol L<sup>-1</sup> is linear in final solution with correlation factor of 0.999. The detection limit of 0.16  $\mu\text{g L}^{-1}$  was obtained based on 3 S<sub>b</sub> (the standard deviation of the blank measurements). In order to evaluate the precision and accuracy of the proposed method, this method was used for the analysis of real water samples. The results are shown in TABLE 3. The efficiency of pre-concentration system was very

good for all tap water samples analyzed, with recoveries close to 100%, indicating that the matrix effect was not significant. The interference study indicates that other types of samples could be analyzed using the proposed procedure. The accuracy and precision of the proposed method was obtained above 97% and R.S.D. ranging from 1- 8%.

TABLE 3 : Determination of cadmium ion in tap water samples (250 mL) with the proposed method.

Sample	Amount of Cd <sup>2+</sup> $\mu\text{g L}^{-1}$		
	Amount added	Amount found	% Recovery ( $\pm$ %RSD)
Tap Water (Tehran)	-	<0.2	-
	1.0	0.92	92 ( $\pm$ 8)
Tap Water (Tehran)	-	<0.2	-
	6.0	5.8	97 ( $\pm$ 4)
Tap Water (Tehran)	-	<0.2	-
	12.0	12.0	100 ( $\pm$ 1)

## CONCLUSION

A simple, sensitive and fast method for preconcentration and determination of trace cadmium in real water samples was established using synthesized mesoporous nanocrystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with high surface area as a sorbent for solid phase extraction. Iso, mesoporous nanocrystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with high surface area is a good alternative for preconcentration of cadmium ions in water samples due to its low cost and active surface sites respect to other available sorbents.

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