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Application of titanium dioxide nanoparticles for preconcentration and determination of As(V)in water samples by graphite furnace atomic absorption spectrometry

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ABSTRACT

Titanium dioxide (TiO_2) nanoparticles were prepared by Sonochemical synthesis method at low intensity and characterized using X-ray diffraction (XRD) and Transmission Electron Microscope (TEM). The preconcentration capability of TiO_2 nanoparticles for As(V) was assessed in this work using column method from aqueous solution prior to their determination by graphite furnace atomic absorption spectrometry(GFAAS). The optimum experimental parameters for preconcentration of As(v), such as pH, volume and flow rate of sample solution, eluent and interfering ions, have been investigated. The adsorption capacity of TiO_2 nanoparticles for As(v) was found to be 32.25 mg g^{-1}. Also the method detection limit, precision (R.S.D., n=8) and enrichment factor for As(v)were 72 ng L^{-1} , 5.3 % and 83, respectively. The method has been applied for the determination of trace element in some environmental water samples with satisfactory results.

Keywords:Preconcentration, As(V), Titanium Dioxide Nanoparticles, Microcolumn separation, Adsorption capacity, GFAAS

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INTRODUCTION

Arsenic is a naturally occurring metalloid and has caused great public concern owing to its ostensible carcinogenicity and harmful health effects. Despite serious safety concerns, arsenic has been extensively used in alloys, glass fire retardants, semiconductors and pharmaceutical products as a part of homeopathic remedies that are used for digestive disorders, food poisoning, sleep problems (insomnia), allergies, anxiety, depression, and obsessive-compulsive disorder (OCD) [1]. Also arsenic in drinking water is an emerging problem and significant levels of arsenic have been reported in groundwater in many areas, such as USA, China, Chile, Bangladesh, Taiwan, Mexico, Argentina, Poland, Canada, Hungary, Japan and India [2]. Exposure to arsenic over several years through the ingestion of contaminated water or food can cause skin, kidney, bladder, and lung cancers as well as neurological and cardiovascular problems[3].

For the determination of inorganic arsenic species in natural waters and regarding the toxicity of this metal and low concentration in aquatic environment[4],initial separation and preconcentration is required before detection by high sensitive analytical techniques. Great varieties of analytical procedures for arsenic separation and preconcentration reported in the literature are usually based on hydride generation[5], solid phase extraction (SPE) [6], cloud point extraction [7], coprecipitation [8], chromatography[9] and capillary electrophoresis[10], etc.

Among these methods, SPE is effective technique for arsenic speciation because of the simple procedure, higher preconcentration factor, rapid phase separation and easy combination with different detection techniques [11, 12]. Various substances have been used as solid phase extraction sorbent for the separation and preconcentration of arsenic species, such as anion exchange resin [6],C18 silica [13], PTFE turnings [14], mesoporous TiO_2[15] and immobilized yeast[16], etc.

The unique properties of nanometer material, in particular as sorbents, have come to fore and promise potentially new solutions to major environmental issues. A consistent body of evidence has shown that nano-sized sorbents are more effective compared to their macro-sized counterparts and attracted much attention due to its special properties due to: (1) the high surface area to mass ratio; (2) high surface reactivity; and (3) unique catalytic activity[17].Recently it has been reported that titanium dioxide nanoparticles has been successfully used for separation and preconcentration of trace metal ions [18, 19].

Thus the present work describes a fast and simple method for extraction, preconcentration and determination of As (V) in water samples based onTiO_2 nanoparticles as a sorbent in SPE procedure supplemented by graphite furnace atomic absorption spectrometry. The results indicate that preconcentration method applied for determination of As (V) has good precision, preconcentration factor, low detection limit and high adsorption capacity. Therefore it could be considered as an efficient technique for analysis of Arsenic (V) in aqueous samples.

MATERIALS AND METHODS

Experimental

Apparatus

All measurements were carried out using a Perkin Elmer AAnlyst 800 graphite furnace atomic absorption spectrometric (Perkin Elmer Instruments, Shelton, CT, USA). The pH values were controlled with a Mettler Toledo 320-S pH meter (Mettler Toledo Instruments Co. Ltd., Shanghai, China) supplied with a combined electrode. Four-channel minipuls3 peristaltic pump (Gilson, Inc., USA) was used in preconcentration process. A self-made PTFE microcolumn (40 mm×3.0mm i.d.), packed with nanometer size TiO_2, was used in all experiments. A minimum length of PVC tubing with an i.d. of 1.0 mm was used for all connection.

Reagents and solutions

A stock solution (1000 $mg.L^{-1}$) of As(V) was obtained by dissolving appropriate amounts ofsodiumsalt heptahydrate ($Na_2HAsO_4{\cdot}7H_2O$)(Merk)in high purity deionized water. Working standard solutions were obtained by appropriate dilution of the stock standard solutions. Titanium tetra-isopropoxide (TTIP) (Merck purity >98%), ethanol (analytical grade) and glacial acetic acid 100% (Merck) were used without any further purification. Glass beads with 40–60 mesh, was purchased from Glass beads Company (Glass beads Co. Tehran, Iran).

Preparation of TiO_2 nanoparticles

The titanium nanoparticles with diameter about 6 nm were prepared following method reported newly by Ghows and Entezari[20]. 50 mL of deionized water and 0.2 mL acetic acid as a dispersant, mixed together In a sonication cell and sonicated. Then 2 mL Titanium tetra-isopropoxide and 5 mL ethanol was injected drop-wise into aqueous solution in 2 min. The mixture was sonicated continuously for 3 h at room temperature condition. The sonication was conducted without cooling so that the temperature was raised from 25 to 75˚C at the end of the reaction. The achieved precipitates were separated by centrifugation (20,000 rpm in 20 min) and washed three times with ethanol and deionized water. The product was dried at 40 C for 24 h. Fig. 1a shows the TEM micrograph of TiO_2 nanoparticles. As we see, the diameter of the particles is estimated to be less than 10 nm. HRTEM image shows that the sample is a single crystal with a growing direction and a step of one atomic layer can be seen (Fig. 1b). The crystallinity of the product is also proven by selected area electron diffraction (SAED) as a crystallographic experimental technique (insert in Fig. 1b).

Fifty milligrams mixture of nanometer TiO_2 including 20 mg of TiO_2 nanoparticles and 30 mg of glass beads with 40-60 mesh was introduced into a PTFE microcolumn (40 mm×3.0 mm i.d) plugged with a small portion of glass wool at both ends.Glass beads were used to facilitate the smooth flow of solution through the column and to probably increase the contact of solution with the surface of the nanoparticles. Before use, 1.0mol L^{-1} HCl solution and doubly distilled water were passed through the column in order to clean and condition it.

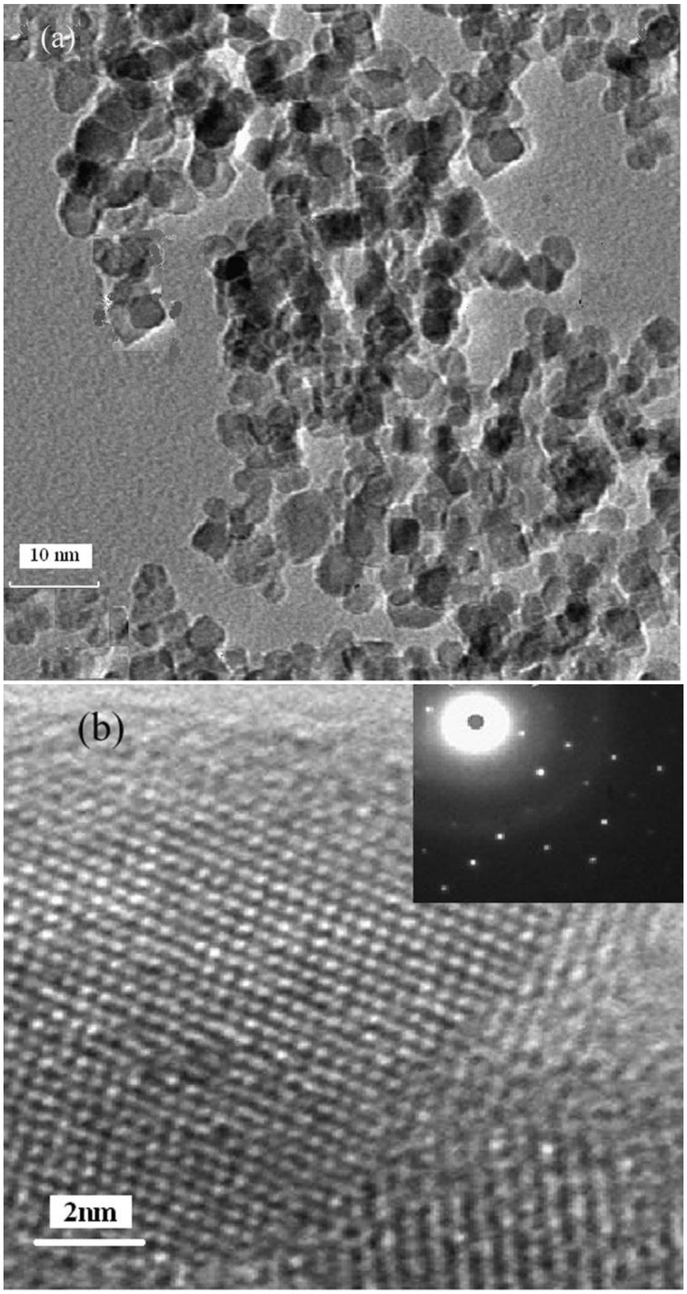

Fig. 1: TEM (1a), HRTEM and SAED (1b) images.2.4 Column preparation

General procedure

The solid-phase extraction procedure for As(V) was as follows: firstly, a portion of aqueous sample solution containing As(V) was prepared and the pH value was adjusted to desired value with 0.1 M HCl and NaOH. Then, the working solution was passed through the column by using a peristaltic pump adjusted to the desired flow rate. When the preconcentration was completed, the retained metal ions on the microcolumn were eluted with 1.5 mL of 0.7 M NaOH solution. The analytes in the effluents were determined by GFAAS. The column could be used repeatedly after regeneration with 1.0 M HCl or HNO_3 solution followed by distilled water. Between the extractions, the minicolumn was dried by passing the air through it for 30min.

RESULT AND DISCUSSION

Effect of pH on adsorption

The pH value plays an important role in adsorption and separation of different ions on adsorption materials. Morterra[21] stated that the pH of solution influences the distribution of active sites on the surface of titanium dioxide nanoparticles. The surface charge is neutral at the isoelectric point (IEP), which is at pH 6.8 for TiO_2 Nanoparticles [22]. In general, when the pH of the solution is lower than the isoelectric point of the adsorbent, the positive charge on the surface provides electrostatic attractions that are favorable for adsorbing anions such as arsenate. In this experiment the effect of the pH on the retention of arsenate on the TiO_2 studied in the range of 1-6 and operated according to the recommended procedure.

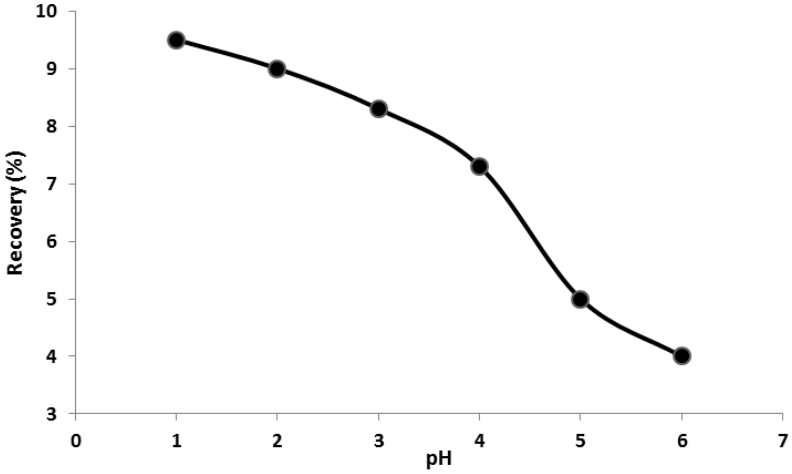

Fig. 2: Effect of pH on the adsorption of As(V) on TiO_2 nanoparticles; As(V): 1.0 µgL^{-1}; sample volume: 50 mL.

Fig.2 shows the results of the effect of pH on the recoveries of arsenateions by nanoparticles, which indicates that the adsorption percentage of the arsenateincreases to the maximum as the pH increases to 1 and decreases with the further increase of pH. Hence, in the following experiments the sample pH was adjusted to 1.

Elution of the adsorbed As (V) ions

It is found from Fig. 2 that the adsorption of arsenite at pH> 4 could be negligible. For this reason, various concentration of NaOHwere considered for the elution of retained As (V) from the microcolumn. Fig. 3 shows the effect of NaOHconcentration on the recovery of the adsorbed As (V).It can be seen that 0.7 M NaOHis enough to recover the As (V) quantitatively. Therefore, we applied 0.7 M NaOHto recover the As (V) from microcolumn in this work. After that we studied the effect of elution volume on the recovery of As (V) by keeping the NaOH concentration equal to 0.7 M. it was found that quantitative recoveries (>95%) could be achieved using 1.5 mL of 0.7 NaOH as eluent.

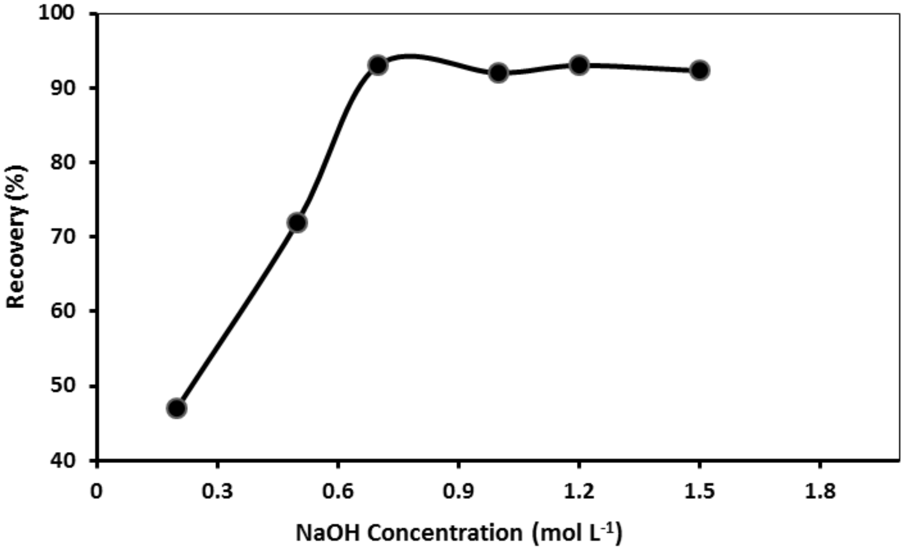

Fig. 3: Effect of NaOH concentration on the recovery of As(V); As(V): 1.0 µgL-1; sample volume: 50 mL; pH:1.

Effect of flow rate of sample solution

The flow rate of sample solution must be another vital factor affecting the preconcentration of As (V) on the nanoparticle as adsorbent and it control the time of analysis. Thus we studied the influence of flow rate of sample solution on retention of As(V)ions in a range of 0.5 to 2.5 mL min^{-1} under the optimum conditions (pH, eluent, etc.) via passing 50 mL of sample solution through the microcolumn by a peristaltic pump. We observed that quantitative recovery (>95%) of As(V)was obtained up to a flow rate of 1.0 mL min^{-1} and the recovery decreased when the flow rate was greater than 1.0 mL min $^{-1}$ due to a decrease in the adsorption kinetics of reaction at higher flow rate. Thus, a flow rate of 1.0 mL min $^{-1}$ was employed for subsequent investigates.

Effect of sample volume

In order to explore the possibilityof enriching low concentrations of analytes from large volumes, the effect of sample volume on the retention ofAs(V) was also investigated. For this purpose a series of sample solution over the range 25-175 mL containing a fixed quantity of As(V) were processed according the recommended procedure. The results were exhibited in Fig. 4.

As can be seen, quantitative recovery (>95 %) of As(V) was obtained for sample volumes of ≤125 mL for As(V) ions. Thus, the adsorbed As(V) can be eluted with 1.5 mL 0.7 mol L^{-1}NaOH, so enrichment factor of 83 was achieved by this method.

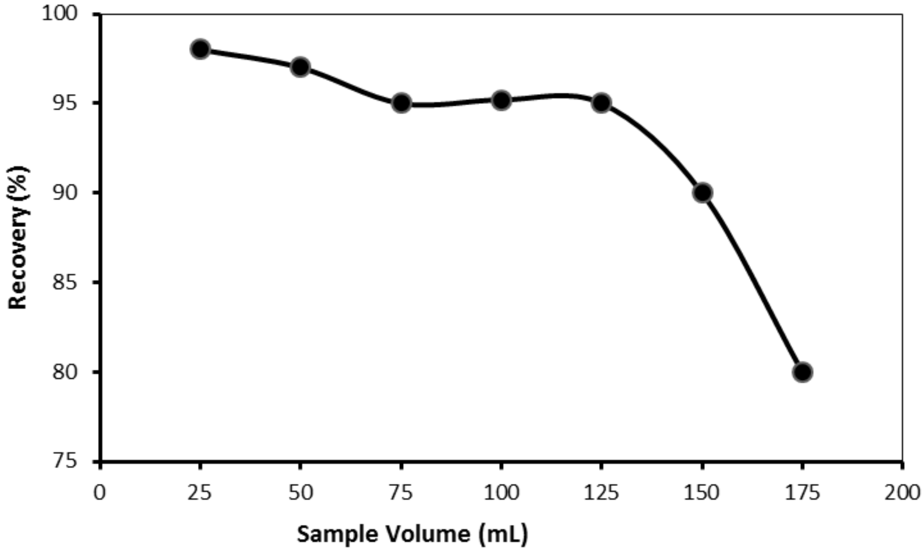

Fig. 4: Effect of sample volume on the adsorption of As(V)on Tio_2 nanoparticles; As(V): 1.0 µgL^{-1}.

Adsorption capacity

Adsorption capacity is one of the important parameters in assessing the adsorption capacity of different adsorbent since it suggests how much adsorbent is required to quantitatively concentrate the analyte from a solution. The capacity study used was adapted from a procedurerecommended by Maquieira et al.[23]. To determine the adsorption capacity, 30 mL aliquots of sample solutions having the different As(V) concentrations (in the range of 0–30 µg mL^{-1}) were adjusted to the appropriate pH with 0.1 mol L^{-1} HCl or NaOH. Then 20 mg of TiO_2 nanoparticles was packed in microcolumn and the preconcentration procedure described above was applied. The amount of As(V) adsorbed at each concentration level was determined. The profile of the adsorption isotherm for As(V) was gained by plotting the concentration (µg mL^{-1}) of As(V) solution versus the milligrams of As(V) adsorbed per gram TiO_2 nanoparticles, and shown in Fig. 5. The result from the adsorption isotherm show that the adsorption capacity of TiO_2 for As(V) was found to be 31.25 mg g^{-1}.

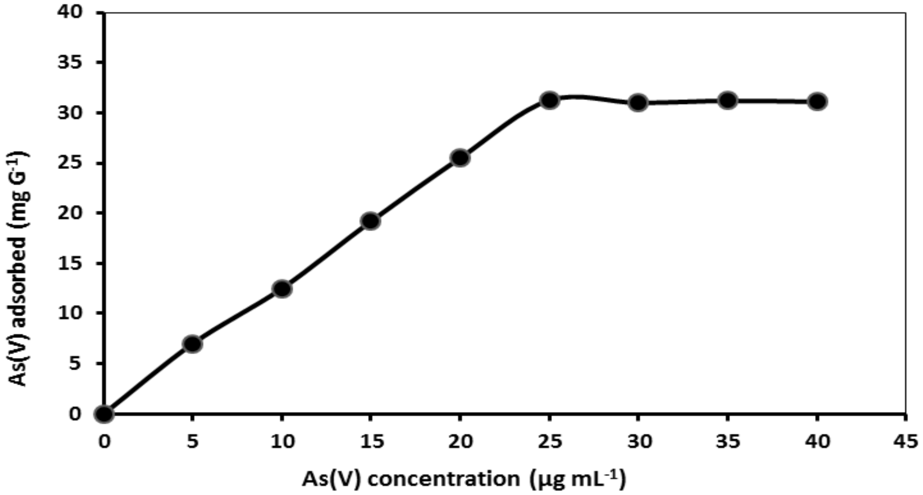

Fig. 5: Adsorption isotherm of As(V) on TiO_2 nanoparticles; Ph:1.0; sample volume 30 mL.

Column reuse

The stability and potential regeneration of the microcolumn packed with TiO_2 nanoparticle were investigated. The column can be reused after regenerated with 10 mL 1.0 mol L^{-1} HCl followed by 20 mL deionized water. After repeating this process 15 times, the recovery of As(V) was still above 95%. Thus the microcolumn packed with TiO_2 nanoparticles can be reused at least 15 times.

Effects of coexisting ions

Generally, the matrix of real environment samples is much complex. The influence of common coexisting ions on the As(V) retention onto TiO_2 nanoparticles was evaluated using the developed method. The existence of coexistence ions would influence the preconcentration of As(V) by competitive adsorption. In these experiments, various foreign cations and anions at various concentrations were added to 1.0μg L^{-1}As(V) at pH 1 and enriched in microcolumn according to the recommended procedure. The tolerance limits of the coexisting ions, defined as the largest amount making the recovery of As(V) less than 95%, were given in Table 1. It can be seen that the presence of coexisting ions at a much higher level has no obvious influence on the adsorption of As(V) ion under the selected conditions.

Table 1. Tolerance limits for coexisting ions for adsorption of As(V) 1.0μg L^{-1}

Coexisting ions	Tolerance limit of ions (Wion/WAs(V))
Fe^{3+}, Ni^{2+}	1000
Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}	1000
Zn^{2+}, Cu^{2+}, Al^{3+}	800
Al^{3+}, Cd^{2+}, Sb^{3+}, Pb^{2+}	700
Cl^{-}, Br^{-}, PO_4^{3-}, NO_3^{-}	700

Analytical performance of the method

The calibration curve for As(V), based on optimal conditions, was linear in the range of 0.45 - 2.1μg L^{-1}. Also in accordance with the definition of IUPAC[24], The detection limit of this method, evaluated as the concentration corresponding to three times the standard deviation of 11 runs measurements of blank solution using the preconcentration method, was found to be 72 ng L^{-1} for As(V). The results (Table 2) show that the precision of this method (RSD), examined by 8 replicate measurements of 1.0μg L^{-1}As(V) in 125 mL of model solutions, was about 5.3% and indicating that the method has good precision for the analysis of trace As(V) ions in solutions samples.

Table 2. Analytical performance of the proposed method toward the As(V) ion

limits of detection (ng L^{-1})	Linear Range (μgL^{-1})	RSD % (n=8)
72	**0.45 – 2.1**	**5.3**

Application of the method on real waters

In order to evaluate the applicability of TiO_2 nanoparticles as SPE adsorbents in the analysis of As(V) in real samples, two environmental water samples (tap water and Mines lake water) were collected from the region of Serdang city in Malaysiaand used for the analysis. In these experiments, the samples were spiked with 1.0 and 2.0 µg L^{-1}As(V) and subjected to the preconcentration procedure. The results (Table 3) indicate that proposed method could be used to determine As(V) in real water samples.

Table 3. Determination of As(V) (µgL^{-1}) in blank and spiked real environmental samples

Samples	Added	Found	Recovery (%)
Tap water	0	0.29 ± 0.13	
	1	1.26 ± 0.09	97
	2	2.25 ± 0.16	98
Mines Lake water	0	0.65 ± 0.11	
	1	1.61 ± 0.15	96
	2	2.63 ± 0.12	99

Also the method has been applied to the determination of As(V) in the standard reference material (JR-1) for its As(V) content. The rock sample (0.5 g) was dissolved in 10 mL of mixture of HF (25 mL), HNO_3 (2 mL) and H_2SO_4 (8 mL) in a Teflon beaker, and heated until 2 mL of solution was remained. 8 mL concentrated HNO_3 was added to this solution and after heating treated with distilled water was added to give a clear solution and was finally made to 100 ml by further addition of distilled water. This solution was analysed for its As content according to the proposed procedure and was determined to be 15.91± 0.06 µg/gr which is in good agreement with its certified value (16.3 µg/gr) with a recovery of 97.5%.

CONCLUSIONS

This paper proved that TiO_2 nanoparticles had excellent enrichment ability for metal elements in water samples. TiO_2 nanoparticles synthesized successfully by Sonochemical method and packed in a micro column as the adsorbent material for preconcentration of As(V) prior to its determination by graphite furnace atomic absorption spectrometry. The results obtained indicate that TiO_2 nanoparticles is an effective SPE sorbent for the adsorption of As(V) from aqueous solutions. The precision and accuracy of proposed method was satisfactory and percentage of As(V) removal from solution is close to 100% at pH 1. Also The TiO_2 nanoparticles show a remarkable adsorption capacity of 31.25 mg g^{-1} for As(V) ions . The method can be successfully applied to the separation, preconcentration and determination of As(V) in environmental samples.

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