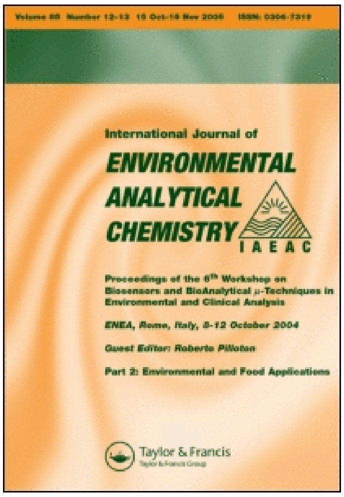

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

# Preconcentration of trace cadmium and manganese using 1-(2-pyridylazo)-2-naphthol-modified $TiO_2$ nanoparticles and their determination by flame atomic absorption spectrometry

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**To cite this Article** Manzoori, Jamshid L. , Amjadi, Mohammad and Hallaj, Tooba(2009) 'Preconcentration of trace cadmium and manganese using 1-(2-pyridylazo)-2-naphthol-modified $TiO_2$ nanoparticles and their determination by flame atomic absorption spectrometry', International Journal of Environmental Analytical Chemistry, 89: 8, 749 — 758

**To link to this Article: DOI:** 10.1080/03067310902736955

**URL:** http://dx.doi.org/10.1080/03067310902736955

*Intern. J. Environ. Anal. Chem.*
Vol. 89, Nos. 8–12, 15 July–15 October 2009, 749–758

# Preconcentration of trace cadmium and manganese using 1-(2-pyridylazo)-2-naphthol-modified $TiO_2$ nanoparticles and their determination by flame atomic absorption spectrometry

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(*Received 27 July 2008; final version received 9 January 2009*)

A new method has been developed for the preconcentration of trace amounts of manganese and cadmium prior to their determination by flame atomic absorption spectrometry (FAAS). The method is based on using a microcolumn packed with 1-(2-pyridylazo)-2-naphthol (PAN)-modified sodium dodecyl sulfate (SDS) coated $TiO_2$ nanoparticles as a solid-phase sorbent. Effects of pH, sample flow rate and volume, elution solution and interfering ions on the recovery of the analytes have been investigated. The adsorption capacity of modified $TiO_2$ nanoparticles was found to be 9.2 and 8.9 $mg\,g^{-1}$ for Mn and Cd, respectively. The detection limits ($3\sigma$) of this method are 1.0 and 0.96 $ng\,mL^{-1}$ for Mn and Cd, respectively. The proposed method has been applied to the determination of the elements in water samples with satisfactory results.

**Keywords:** 1-(2-pyridylazo)-2-naphthol; $TiO_2$ nanoparticle; preconcentration; cadmium; manganese

## 1. Introduction

The determination of traces of cadmium and manganese in various environmental samples is very important because of their effects on human health and the environment. Manganese is nutritionally essential for humans but potentially toxic at higher concentrations. On the other hand, cadmium is known to be highly toxic for animals, plants and humans even at low concentrations and can be accumulated in several organs. The most important anthropogenic sources of cadmium include emissions from industrial plants, such as zinc smelters, steel works, incinerators and power stations and of manganese include mining of ore, battery manufacture, steel industries and pesticides. Distribution of these elements from above sources may lead to local contamination and hence health problems. Therefore, there is an increasing need to monitor trace levels of these elements in the environmental samples. For this purpose, very sensitive, simple, rapid and inexpensive methods are necessary. The direct determination of extremely low concentrations of trace elements by modern atomic spectroscopic methods, such as atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) is often difficult. The limitations arise from the insufficient sensitivity of these techniques as well as the matrix interferences. For this reason,

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ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310902736955
http://www.informaworld.com

the preliminary separation and preconcentration of trace elements from matrix is often required.

The most widely used techniques for the separation and preconcentration of trace elements include liquid–liquid extraction [1,2], solid phase extraction (SPE) [3–14], co-precipitation [15–17], ion-exchange [18,19] and electrochemical deposition [20]. Recently, more attention has been paid to SPE technique due to having several advantages over the classical liquid–liquid extraction technique. These include higher preconcentration factor, rapid phase separation and the ability of combination with different detection techniques in on-line or off-line mode. Numerous substances have been proposed and applied as solid phase extractants, such as modified silica [3,4] and alumina [5], magnesia [6], active carbon [7,8], chelating resins [18,19] and cellulose [9,10].

Nanomaterials are new solid materials that are gaining importance in recent years due to their special properties [21]. They are clusters of atoms or molecules of metal and oxide, ranging in size from 1 nm to almost 100 nm, falling between single atoms or molecules and bulk materials. One of the important properties of nanoparticles is that most of the atoms are on the surface of these materials. The surface atoms are unsaturated, and can therefore bind with other atoms [22]. Consequently, the nanometer materials usually have high chemical activity and adsorption capacity.

Nanometer $TiO_2$ [22–31], $Al_2O_3$ [32–34], $ZrO_2$ [35,36] and $CeO_2$ [37] have been used as sorbents of SPE for preconcentration of metal ions from various samples. The adsorption properties of these oxides, including nanometer $TiO_2$, depend on the factors such as their crystal structure, morphology, defects, specific surface area, hydroxyl coverage, surface impurities and modifiers. Chemical or physical modification of the sorbent surface usually leads to improvements of its properties, specially its selectivity and/or affinity towards ions. The most common modifiers are chelating agents, which are used to load the surface with some donor atoms such as oxygen, nitrogen, sulphur and phosphorus. These donor atoms are capable of selective binding with certain metal ions.

It is well known that surfactant molecules can form self-aggregates called ‘admicelles’ or ‘hemimicelles’ on solid alumina surfaces. Insoluble hydrophobic compounds such as many chelating agents can be solubilised in hydrophobic core of these aggregates [38,39]. Several reports have been appeared about modification of alumina by using the surfactants as mediator and chelating agents as modifier [40–42]. However, the use of this method for the modification of $TiO_2$ and its nanoparticles is rare [43]. In the present work, 1-(2-pyridylazo)-2-naphthol (PAN) has been immobilised on sodium dodecyl sulfate (SDS)-coated $TiO_2$ nanoparticles. The modified nanometer $TiO_2$ has been applied to the preconcentration of traces of cadmium and manganese from environmental samples.

## 2. Experimental

### 2.1 *Apparatus*

A Shimadzu (Kyoto, Japan) Model AA-670G atomic absorption spectrometer with deuterium lamp background correction was used for the determination of manganese and cadmium. Manganese and cadmium hollow cathode lamps (operated at 5 and 4 mA, respectively) were used as the radiation sources at the wavelengths of 228.8 and 270.5 nm, respectively.

A Garant ultrasonication bath Model XB6 was used to reduce the aggregation of $TiO_2$ nanoparticles. The pH values were measured with a Metrohm model 654 pH Meter.

Shimadzu (Kyoto, Japan) Model SJ-1112 peristaltic pumps were used in the preconcentration process.

### 2.2 *Reagents*

All chemicals were of analytical grade and all solutions were prepared with triply distilled/deionised water (obtained from Ghazi Serum Company, Tabriz, Iran). 1-(2-Pyridylazo)-2-naphthol and SDS was purchased from Merck. Nanometer $TiO_2$ 99.9% was obtained from Aldrich. The average diameter of nanoparticles was in the range of 25–70 nm and the specific surface area determined by the BET method was 20–25 $m^2\,g^{-1}$. Standard stock solutions of Cd and Mn (1 $mg\,mL^{-1}$) were prepared by dissolving appropriate amounts of analytical grade $Cd(NO_3)_2 \cdot 6H_2O$ and $Mn(NO_3)_2 \cdot 4H_2O$ in distilled water and further diluted daily prior to use.

### 2.3 *Preparation of PAN-modified $TiO_2$ nanoparticles*

The modification procedure was adopted from a published method [43]. To a 150-mL beaker, 1 g of $TiO_2$ and 20 mL of 0.001 $mol\,L^{-1}$ HCl were added under ultrasonic action to reduce the aggregation of nanoparticles. To maintain a relatively constant ionic strength, 0.3 mL of 1 $mol\,L^{-1}$ $KNO_3$ was added drop wise. The pH of the solution was adjusted to 5 using either 0.1 $mol\,L^{-1}$ $HNO_3$ or 0.1 $mol\,L^{-1}$ $NH_3$. Then 3 mL of 1 $mol\,L^{-1}$ SDS was added (the final concentration of SDS reached 7.5 $mmol\,L^{-1}$). The solution was stirred for 1 h by means of a magnetic stirrer, then 0.2 g of PAN was placed into the solution and the mixture was further stirred for 1 h at 60°C in a water-bath. The resultant suspension was filtered and dried under vacuum to obtain a fine orange powder.

### 2.4 *General procedure*

A homogenous mixture of 20 mg of nanometer $TiO_2$–PAN and 50 mg of glass beads were filled into a microcolumn (45 mm × 2.5 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, 50 mL doubly distilled deionised water was passed through the microcolumn in order to equilibrate, clean and neutralise it. A 50 mL portion of standard or sample solutions containing Cd (5–200 $ng\,mL^{-1}$) and Mn (5–150 $ng\,mL^{-1}$) were prepared, and the pH value was adjusted to the desired pH (7 for Cd and 8.5 for Mn) using phosphate buffer. Each solution was passed through the microcolumn at a flow rate of 1.0 $mL\,min^{-1}$ using a peristaltic pump. Later, the metal ions retained on the microcolumn were eluted with 1.5 mL of 0.1 $mol\,L^{-1}$ $HNO_3$ solution. The analytes were then determined by flame atomic absorption spectrometry (FAAS).

### 2.5 *Sample preparation*

Rain and spring waters were collected from Tabriz and Mirabad spring (Nagadeh, Iran), respectively. After sampling, they were filtered through Round filter paper (blue band, No. 300210) to remove suspended particulate matter. Mineral waters were obtained from local sources.

## 3. Results and discussion

### 3.1 *Modification of $TiO_2$ nanoparticles with PAN*

It is known that $TiO_2$ surface in water at pH values below 6.2, the isoelectric point [23], possesses a positive charge and therefore is hydrophilic and not favourable for the adsorption of hydrophobic organic compounds. However, it can strongly adsorb the negatively charged SDS molecules in acidic solution. Columbic interactions are the primary forces responsible for adsorption of anionic surfactants at low concentrations. As the surfactant concentration is gradually increases, SDS molecules aggregate on the surface through Van Der Waals interactions at the hydrocarbon tails of the molecules. These surface aggregates are called hemimicelles or admicelles. In a hemimicelle, the head groups (ionic ends) of the surfactants are anchored in the nanometer $TiO_2$ surface, and the hydrocarbon chains point towards the aqueous phase. As a result of the formation of hemimicelles, the nanometer $TiO_2$ surface gains a hydrophobic characteristic [43]. In this work the concentration of SDS was fixed at $7.5\,\mathrm{mmol\,L^{-1}}$, which is below its critical micellar concentration (CMC). Above the CMC micelles of SDS will be formed in solution, which are not adsorbed on $TiO_2$ surface. When PAN is added to SDS-coated $TiO_2$ nanoparticles, hemimicelles or admicelles can homogeneously trap molecules of PAN via the interactions between the hydrophobic groups in the PAN and the exposed hydrocarbon tails in the hemi-micelles. This causes $TiO_2$ nanoparticles to change colour from white to orange. Since the hydrophilic groups of PAN are oriented towards the aqueous phase, metal ions can easily be adsorbed on the nanometer $TiO_2$–PAN surface. It should be mentioned that in our experimental conditions PAN could not be coated on pure $TiO_2$ nanoparticles without adding SDS.

### 3.2 *Effect of variables on sorption and elution of ions*

In order to establish the best conditions for sorption and elution of cadmium and manganese, the influence of several variables was studied and optimised.

Among the factors affecting analytes sorption, pH is the most critical one. The effect of sample pH on the sorption of Cd and Mn was investigated in the range of 4–10. As shown in Figure 1, Cd and Mn could be adsorbed quantitatively (recovery $>95\%$) at pH 7.0 and 8.5, respectively. The decrease in retention of ions at lower pHs is due to incomplete chelate formation and its sorption on microcolumn.

As the retention of elements on microcolumn depends upon the flow rate of the sample solution, its effect was examined by passing 50 mL of sample solution through the microcolumn with a peristaltic pump. The flow rates were adjusted in a range of $0.5–3.0\,\mathrm{mL\,min^{-1}}$. As shown in Figure 2, quantitative recoveries of studied metal ions were obtained at flow rates $\leq 1.0\,\mathrm{mL\,min^{-1}}$. However, the recoveries of the metal ions will decrease with further increasing of the flow rate from $1.0\,\mathrm{mL\,min^{-1}}$, due to a decrease in the adsorption kinetics at a high flow rate. Thus, a flow rate of $1.0\,\mathrm{mL\,min^{-1}}$ is selected in this work.

To explore the possibility of enriching low concentrations of ions from a large volume, the effect of sample volume on the retention of Cd and Mn was also investigated by varying the sample volume from 25 to 200 mL containing 25 μg of each ion. The results in Figure 3 show that quantitative recoveries of both analytes could be achieved when the sample volume was less than 50 mL.

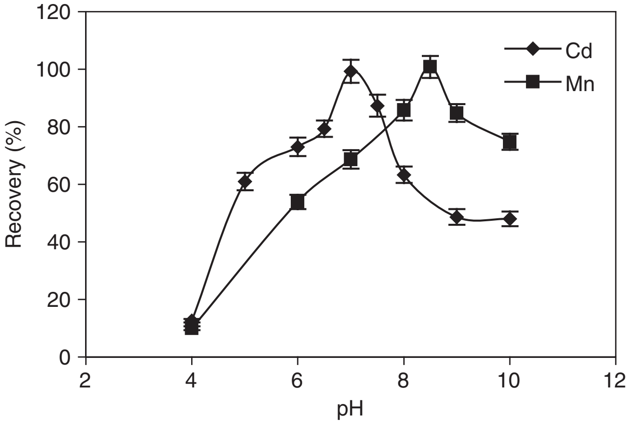

Figure 1. The effect of pH on the sorption of the studied elements on the modified nanometer $TiO_2$, Mn: 50 ng mL$^{-1}$; Cd: 50 ng mL$^{-1}$; sample volume: 50 mL.

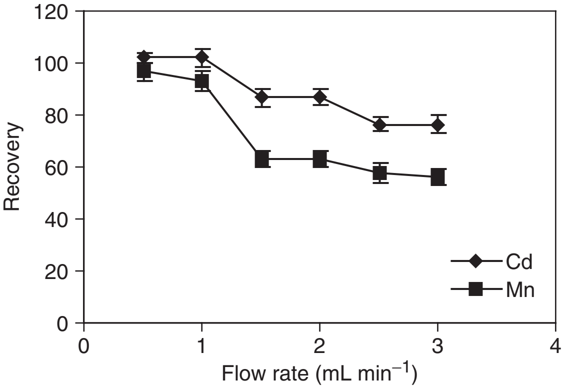

Figure 2. The effect of flow rate of sample solutions on the sorption of the studied ions on the modified nanometer $TiO_2$, Mn: 50 ng mL$^{-1}$ pH, 8.5; Cd: 50 ng mL$^{-1}$ pH, 7; sample volume: 50 mL.

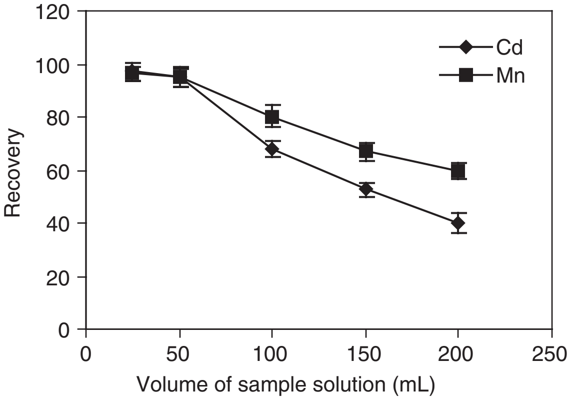

Figure 3. The effect of the sample volume on the sorption of metal ions on the modified nanometer $TiO_2$; the conditions are the same as Figure 2.

Elution conditions were also optimised to achieve the maximum recovery of adsorbed ions. In acidic medium almost no sorption of ions occurred on PAN-modified nanometer-sized $TiO_2$ probably because of instability of PAN-modified $TiO_2$. Therefore, acidic solution can be applied for elution of microcolumn. In this study, $HNO_3$ solution was selected as eluent for desorption of the retained analytes. It should be mentioned that a separate column should be used for each experiment.

The effect of volume, concentration and flow rate of eluent was optimised. Table 1 indicates the influences of two latter parameters. According to the results, the $HNO_3$ concentration of $0.1\,mol\,L^{-1}$ and the elution flow rate of $1.0\,mL\,min^{-1}$ were selected as suitable values. The influence of eluent volume on the recovery of ions is shown graphically in Figure 4. As can be seen the minimum amount of $HNO_3$ required to obtain quantitative recovery of ions is 1.5 mL. So, this value was selected as optimum volume.

### 3.3 *Adsorption capacity*

The adsorption capacity of modified nanometer-sized $TiO_2$ for analytes is an important parameter since it suggests how much adsorbent should be used. In order to determine the adsorption capacity, 10 mL of each metal ions solution at concentration of $20\,\mu g\,mL^{-1}$ was

Table 1. Optimisation data for elution of the analytes adsorbed on PAN-modified nanometer $TiO_2$.

| | Recovery (%) | | | Recovery (%) | |
|---|---|---|---|---|---|
| Eluent flow rate ($mL\,min^{-1}$) | Cd | Mn | Eluent concentration ($mol\,L^{-1}$) | Cd | Mn |
| 0.5 | 98.4 | 95.3 | 0.05 | 89.1 | 86.4 |
| 1 | 102.3 | 103.3 | 0.1 | 98.5 | 100.7 |
| 1.5 | 104.0 | 96.9 | 0.5 | 96.9 | 100.7 |
| 2 | 98.7 | 103.3 | 1 | 102.7 | 98.6 |

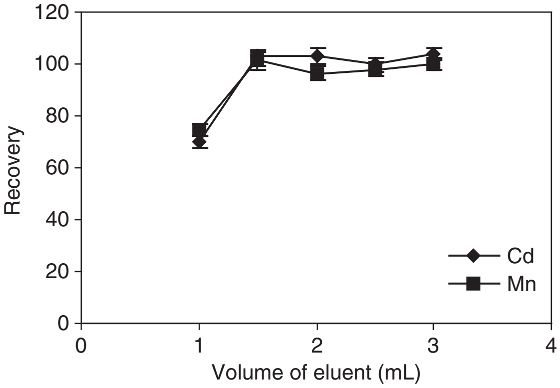

Figure 4. The effect of volume of $0.1\,mol\,L^{-1}$ $HNO_3$ on the recovery of adsorbed ions. The conditions are the same as Figure 2.

prepared and adjusted to desired pH. Then 20 mg of sorbent was added and the solution was stirred for 1 h. The amount of metal ion remained in the solution was determined by FAAS after centrifugation. The results showed that the modified nanometer-sized $TiO_2$ had an adsorption capacity of 8.9 and 9.2 mg g$^{-1}$ for Cd and Mn, respectively.

### 3.4 *Study of interferences*

The interferences of co-existing ions in the determination of 50 ng mL$^{-1}$ of Cd and Mn (50 mL) were studied individually by the proposed procedure under optimum conditions. A foreign ion was considered to interfere when it caused a determination error of more than 5%. The results obtained are summarised in Table 2. At the given concentrations, no interference was observed in the determination of elements at trace levels.

### 3.5 *Detection limits and precision*

The detection limits according to the definition of IUPAC ($3S_b/b$ where $S_b$ is the standard deviation of blank and $b$ is the slope of calibration graph) [44] are 0.96 and 1.0 ng mL$^{-1}$ for Cd and Mn, respectively. A study of precision was performed by carrying out five independent measurements of solutions of each ion at 50 ng mL$^{-1}$. The relative standard deviations (RSDs) are 4.5 and 3.5% for Cd and Mn, respectively.

### 3.6 *Application*

The proposed method was applied to the analysis of several natural water samples. The reliability of the method was checked by spiking the samples and comparing the

Table 2. Tolerance limits for foreign ions in the determination of 50 ng mL$^{-1}$ Cd and Mn.

| | Tolerance limit (ng mL$^{-1}$) | |
|---|---|---|
| Foreign ion | Mn | Cd |
| $Na^+$ | 25,000 | 50,000 |
| $K^+$ | 25,000 | 25,000 |
| $Mg^{2+}$ | 5000 | 50,000 |
| $Cl^-$ | 50,000 | 50,000 |
| $Ca^{2+}$ | 2000 | 5000 |
| $SO_4^{2-}$ | 25,000 | 25,000 |
| $PO_4^{3-}$ | 50,000 | 50,000 |
| $F^-$ | 25,000 | 50,000 |
| $NO_3^-$ | 25,000 | 25,000 |
| $Fe^{3+}$ | 250 | 250 |
| $Al^{3+}$ | 250 | 500 |
| $Pb^{2+}$ | 2000 | 5000 |
| $Mn^{2+}$ | – | 5000 |
| $Cd^{2+}$ | 250 | – |
| $Zn^{2+}$ | 500 | 500 |
| $Cu^{2+}$ | 250 | 5000 |
| $Cr^{3+}$ | 2500 | 250 |
| $Co^{2+}$ | 250 | 10,000 |
| $Ni^{2+}$ | 2000 | 2000 |

Table 3. Determination of cadmium and manganese in water samples (results of recoveries of spiked samples).

| Sample/Element | Added ($ng\,mL^{-1}$) | Found ($ng\,mL^{-1}$)[a] | Recovery (%) | ETAAS |
|---|---|---|---|---|
| Rain water | | | | |
| Mn | 0 | nd | – | nd |
| | 20 | $19.1 \pm 0.5$ | 95.4 | $20.7 \pm 1.0$ |
| | 50 | $50.6 \pm 1.1$ | 101.2 | $49.6 \pm 2.3$ |
| Cd | 0 | nd | – | nd |
| | 20 | $19.7 \pm 0.6$ | 98.6 | $19.1 \pm 0.7$ |
| | 50 | $50.9 \pm 1.9$ | 101.8 | $51.6 \pm 1.3$ |
| Vata mineral water | | | | |
| Mn | 0 | nd | – | nd |
| | 20 | $19.6 \pm 1.0$ | 97.8 | $19.6 \pm 0.1$ |
| | 50 | $49.7 \pm 1.1$ | 99.4 | $51.2 \pm 1.8$ |
| Cd | 0 | nd | – | nd |
| | 20 | $20.2 \pm 0.6$ | 101.1 | $19.3 \pm 0.5$ |
| | 50 | $50.9 \pm 2.8$ | 101.8 | $51.9 \pm 0.5$ |
| Sahand mineral water | | | | |
| Mn | 0 | nd | – | nd |
| | 20 | $19.8 \pm 0.8$ | 99.1 | $20.3 \pm 0.3$ |
| | 50 | $49.8 \pm 1.9$ | 99.7 | $50.8 \pm 1.5$ |
| Cd | 0 | nd | – | nd |
| | 20 | $20.9 \pm 0.9$ | 102.8 | $19.3 \pm 0.6$ |
| | 50 | $51.9 \pm 2.8$ | 101.9 | $50.5 \pm 1.1$ |
| Mirabad spring water | | | | |
| Mn | 0 | nd | – | nd |
| | 20 | $19.5 \pm 0.5$ | 97.8 | $20.6 \pm 0.4$ |
| | 50 | $51.4 \pm 1.4$ | 102.9 | $50.9 \pm 0.5$ |
| Cd | 0 | nd | – | nd |
| | 20 | $20.0 \pm 0.8$ | 100.1 | $18.7 \pm 1.2$ |
| | 50 | $51.4 \pm 3.2$ | 102.9 | $50.4 \pm 4.0$ |

Note: nd: not detected.

[a] Averages of three determinations ± standard deviation.

results with data obtained by electrothermal atomic absorption spectrometry (ETAAS). The results are summarised in Table 3. The proposed method gave satisfactory average recoveries (95 and 103%) and there is good agreement between the obtained results by this method and those of ETAAS at 95% confidence level.

## 4. Conclusions

1-(2-Pyridylazo)-2-naphthol (PAN) was successfully immobilised on nanometer $TiO_2$ via coating with SDS. The modified $TiO_2$ nanoparticles were used for preconcentration of cadmium and manganese prior to their determinations by FAAS. The modification procedure is relatively simple and rapid and the prepared sorbent has good capacity and appropriate selectivity towards investigated ions. In Table 4 the adsorption capacity of the prepared sorbent has been compared with some other sorbents reported in literature. As can be seen the capacity of PAN-modified $TiO_2$ nanoprticles is higher than pure $TiO_2$ or immobilised $TiO_2$ nanoparticles. As the aim of this work was the determination of

Table 4. Comparison of adsorption capacities (mg $g^{-1}$).

| Sorbent | Cd | Mn |
|---|---|---|
| Nanometer $TiO_2$ [22] | – | 2.14 |
| Nanometer $TiO_2$ immoblised on silica gel [29] | 2.93 | 2.47 |
| Nanometer $ZrO_2$ [36] | – | 1.3 |
| Multiwalled carbon nanotube [45] | 7.42 | 4.86 |
| Nanometer alumina-chromotropic acid [34] | 10.3 | 15.1 |
| Nanometer $TiO_2$–PAN [This work] | 8.9 | 9.2 |

Cd and Mn in water samples, the proposed method was successfully applied to the monitoring of traces of these elements in water sample solutions. The precision and accuracy of the method are satisfactory. However, the method seems to be applicable to the preconcentration of other transition metal ions.

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