



Application of Modified Nano Alumina as a Solid Phase Extraction Sorbent for the Separation and Preconcentration of Manganese (II) in Milk and Water Samples and its Determination by Flame Atomic Absorption Spectrometry

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ABSTRACT

A simple, selective and efficient solid phase extraction method based on the use of γ -alumina nanoparticles coated with sodium dodecyl sulfate (SDS) and modified with 2-(5-Bromo-2-pyridylazo)-5-(diethylamino) phenol (5-Br-PADAP) as a new adsorbent was developed for the separation and preconcentration of trace amounts of manganese (II) prior to determination by flame atomic absorption spectrometry. Analytical influencing parameters including pH value, amount of modified sorbent, equilibrium time, volume and concentration of eluent were examined. Under the optimum conditions, adsorption capacity of nano- Al_2O_3 -SDS-5-Br-PADAP, enrichment factor and limit of detection for manganese (II) was 18.5 mg g^{-1} , 25 and $0.9 \mu\text{g L}^{-1}$, respectively. The procedure was successfully applied to the determination of manganese (II) in water and milk samples.

KEYWORDS: γ -Alumina nanoparticles; Manganese (II); Preconcentration; Water and Milk samples; FAAS.

1. INTRODUCTION

Manganese is necessary for the proper function of several enzymes and is an essential micro-nutrient for the function of the brain, nervous system, and normal bone growth. It is present in large quantities in various steel materials as a hardening agent. It also finds application in pharmaceutical preparations. However, excessive intake can cause lesions, headache, psychotic behavior, drowsiness and other related symptoms and/or diseases. Thus, manganese is an important element from an environmental perspective [1]. Therefore, the determination of trace amounts of manganese in several matrices is very important for some areas, such as environmental chemistry and food control [2, 3]. In general, concentrations of manganese in fresh waters range from 0.02 to $130 \mu\text{g L}^{-1}$ [4]. Therefore, the determination of this metal as Mn^{2+} ion often requires a method offering low detection limits. Although atomic spectrometric methods are powerful analytical tools for the determination of trace elements in environmental samples, preconcentration techniques combined with AAS are still necessary [5]. Liquid-liquid extraction (LLE) [6-8], solid phase extraction (SPE) [9] and cloud point extraction (CPE) [10-13] have been widely used for the preconcentration of manganese from water samples prior to its determination by flame atomic absorption spectrometry.

Among these procedures, the most commonly used method is solid phase extraction, which provides advantages such as preconcentration of trace metals from a larger sample volume, reduction or elimination of matrix interference. Many methods based on different SPE sorbents have been used for the preconcentration of metals. The main requirements for a substance to work effectively as a SPE adsorption material are as follows: it should consist of stable and insoluble porous matrix having suitable active groups, typically organic groups, which can interact with analytes; it should achieve fast and quantitative sorption; and it should have high adsorption capacity, good regenerability and surface area accessibility. Therefore, many adsorbents, such as ion exchange resins [14], molecular imprinted polymers (MIPs) [15], functionalized activated carbon [16, 17], chemically bonded multiwall carbon nanotubes [18], metal oxides [19], metal oxide nanoparticles (such as titania, zirconia, silica and alumina [20]) and biomaterials [21] have been widely employed as SPE sorbent materials. Among these sorbents, nanometer-sized materials have gained more attention in recent years due to their special properties [22]. One of the most interesting properties is that most atoms are on the surface of the nanoparticles. The unsaturated surface atoms can bind with other atoms possessing strong

chemical activities which produce a high adsorption capacity [23].

Nano-alumina, because of its versatile properties including excellent mechanical strength, inertness to most acids and alkalis [24], high adsorption capacity [22], large specific surface area [25–27] and absence of internal diffusion resistance [28], have been successfully applied for the separation and preconcentration of trace heavy metal ions. Furthermore, functional groups such as oxygen, nitrogen, phosphorus and sulfur are able to form the selective binding with both nano-alumina and certain metal ions [25].

Metal chelates could provide higher selectivity and high enrichment factors for such a preconcentration and separation. In the present work, we modified the nano alumina with sodium dodecyl sulfate (SDS) and 2-(5-Bromo-2-pyridylazo)-5-(diethylamino) phenol (5-Br-PADAP) as a new sorbent for the preconcentration of manganese (II) from water and milk samples prior to determination by flame atomic absorption spectrometry.

2. EXPERIMENTAL

2.1. Apparatus

A PG-990 (PG instrument Ltd., United Kingdom) atomic absorption spectrophotometer, equipped with deuterium background correction, manganese hollow cathode lamp and an air-acetylene flame was used for manganese determination. All data acquisition was made according to peak height with the equipment software. The operating conditions were: wavelength 279.5 nm, spectral resolution 0.4 nm, applied lamp current 5.0 mA, air flow rate 10.0 L min⁻¹ and acetylene flow rate 1.3 L min⁻¹. A Hettich centrifuge (Model Universal 320R, Germany) was used for centrifugation. The pH values were measured with a Metrohm pH-meter (model: 827) supplied with a glass-combination electrode.

2.2. Reagents and materials

All reagents used were of analytical reagent grade. Deionized water was used throughout the experiments. A stock 1000 mg L⁻¹ of manganese was prepared by dissolving an appropriate amount of Mn(NO₃)₂·4H₂O (Merck, Darmstadt, Germany) in 1% nitric acid solution. The working solutions of manganese were made by suitable dilution of the stock solution with deionized water. 2-(5-Bromo-2-pyridylazo)-5-(diethylamino) phenol (5-Br-PADAP) purchased from Merck (Darmstadt, Germany). Fresh 0.01 mol L⁻¹ solution of 5-Br-PADAP was prepared daily by dissolving an appropriate amount of reagent in 95% ethanol. Nano γ -alumina (Aluminum oxide, gamma-phase, 99% (metals basis), Alfa Aesar, MA, USA) was activated by shaking with 4 mol L⁻¹ nitric acid and washing two times with deionized water. Sodium dodecyl sulfate (SDS) (Merck, Darmstadt, Germany) was used without further purification. A buffer solution (pH 10.0, 1.0 mol L⁻¹) was prepared by mixing an appropriate amount of ammonia solution with ammonium chloride solution. Pipettes

and glass vessels used for trace analysis were stored in 10 % nitric acid for at least 24 h and washed four times with deionized water before use.

2.3. Preparation of nano γ -Al₂O₃ modified with 5-Br-PADAP

2 g of activated nano γ -alumina was added to 50 mL solution containing 100 mg SDS and 2 mL 5-Br-PADAP solution in a 100 mL flask. The pH of the solution was adjusted to 2–3 with dilute solutions of HNO₃ and NaOH while stirring the suspension with a stirrer. After mixing for 15 min, the supernatant solution was discarded and modified nanometer-sized γ -alumina was filtered off and washed with deionized water and then dried at room temperature for 24 h.

In order to measure the amount of 5-Br-PADAP loaded on the SDS- Al₂O₃, a portion of the supernatant solution was diluted to the appropriate volume and the absorbance of the solution was measured at maximum wavelength (445 nm for 5-Br-PADAP). Comparisons of the absorbance of supernatant solution with absorbance of initial ligand solution at similar conditions indicate the amount of ligand loaded on SDS-Al₂O₃. Ligand molecule entrapped in the interior core of the admicelles formed on the alumina surface lead to change in alumina color indicating ligand immobilization on SDS- Al₂O₃. It was found that 85% of 5-Br-PADAP was adsorbed on the SDS coated on alumina.

2.4. Preparation of the real samples

A 10 ml portion of milk sample was placed in a 100 ml beaker and 10 ml of 65% HNO₃ and 3 ml of 30% H₂O₂ were added. The contents in the beaker were heated on a hotplate at 100 °C for 40 min. Most of the acids were evaporated and then the residue was dissolved with 10 ml of 1.0 mol L⁻¹ HCl [29]. The obtained clear solution was neutralized by adding solid NaOH and diluted in a 25 ml volumetric flask. A 10 ml portion of final solution was analyzed according to the prescribed procedure.

All of the collected water samples (tap, mineral, river, and sea water) were filtered through a cellulose membrane filter (Millipore) of pore size 0.45 μ m and after acidification to 1% with concentrated nitric acid, were stored in polyethylene bottles.

2.5. Recommended procedure

The adsorption of manganese (II) by modified nano alumina was studied by a batch operation at room temperature. The batch mode adsorption was selected owing to its simplicity. The general procedure for the extraction of this ion by modified nano alumina was as follows: an aliquot of 25 mL sample solution containing manganese (II) ions and 100 mg of modified nano alumina were prepared and the pH value was adjusted to 10.0 with ammonia buffer solution. The mixture was shaken manually for about 1 min. After that, the test tube was placed in a centrifuge and separation of sorbent was achieved by centrifugation for 5 min at 9000 rpm. The aqueous phase was easily decanted by

inverting the tube. Desorption of manganese (II) ions was performed by adding 1.0 mL of ethanol solution containing 1.0 mol L⁻¹ HNO₃ to the sorbent. After manual shaking for about 1 min, the sorbent was separated by centrifugation (3 min at 9000 rpm) and the concentration of manganese was determined by FAAS.

3. RESULTS AND DISCUSSION

In order to obtain highly sensitive, accurate and reproducible results, analytical parameters including pH, type and volume of eluent solution, amount of sorbent and equilibrium time were optimized for the preconcentration of manganese (II) ions.

3.1. The Effect of pH

The adsorption of SDS on alumina is highly dependent on the solution pH. Negatively charged SDS was more effectively and nearly quantitatively retained (about 99%) on the positively charged alumina surfaces at pH 1–4 via formation of self-aggregates [26, 30]. This phenomenon greatly increases by decreasing the pH due to the higher charge density on the mineral oxide surface. In the preliminary studies, it was found that when 5-Br-PADAP was mixed with SDS coated on alumina nanoparticles, the ligand got trapped homogeneously on the hemi-micelles or ad-micelles formed by SDS on alumina surface in a manner similar to that demonstrated for the other organic ligands [31–35] and the color of alumina changed from white to orange. A suggested binding mode of SDS-5-Br-PADAP to nano-alumina surface and the manganese (II) ions adsorption have been showed in Fig. 1.

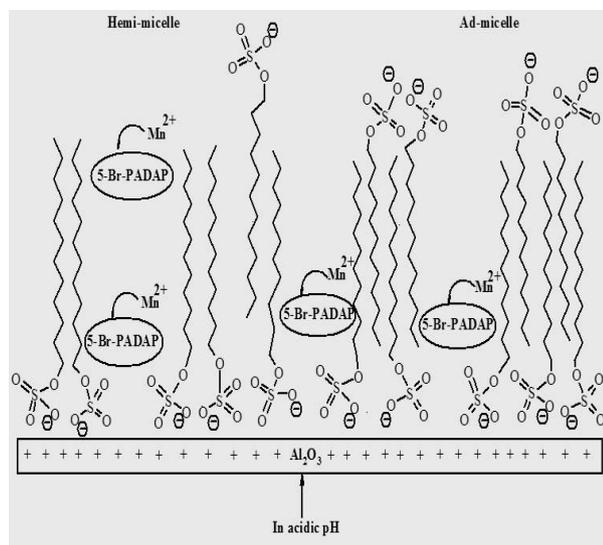


Fig. 1. A suggested binding mode of SDS-5-Br-PADAP on nano-alumina surface.

One of the most important factors in a solid phase extraction procedure is the pH of the aqueous phase for the quantitative recoveries. The dependence of metal sorption on pH is related to both the metal chemistry in the solution and the ionization state of the functional groups of the sorbent which affect the availability of binding sites [36, 37]. For investigating the effect of

pH on manganese ions recovery, a set of similar experiments in the pH range of 2–12 has been carried out and respective results are depicted in Fig. 2. The initial pH of the solution was adjusted by the addition of concentrated solutions of HNO₃ or NaOH and measured by a calibrated pH meter. As can be seen, the optimum pH range for quantitative recoveries of manganese (II) on modified adsorbent is 9–12. The decrease in recovery at pH values lower than 9 may be due to the competition of proton with analyte in binding to donor atoms. Therefore, a pH of 10.0 was selected for subsequent work and in all experiments the pH of the solution was fixed at pH 10.0 with ammonium chloride/ammonium hydroxide buffer solution.

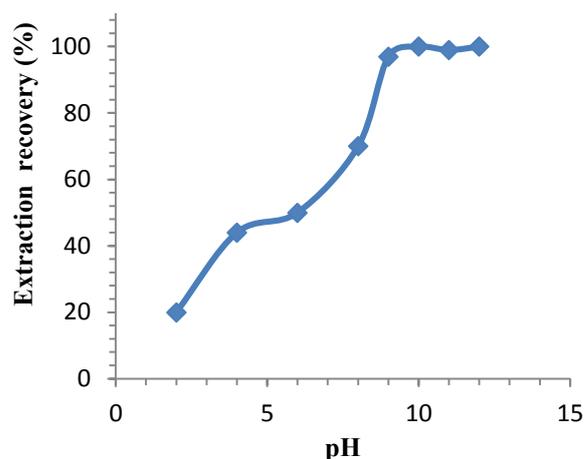


Fig. 2. Effect of pH on the extraction recovery. Conditions: sample volume: 25 mL, manganese concentration: 100.0 μg L⁻¹, amount of modified sorbent: 100 mg, eluent: 1.0 ml of 1.0 mol L⁻¹ of HNO₃ in ethanol.

3.2. Choice of eluent: type, concentration and volume

Desorption of the adsorbed material on the solid phases is an important step in the solid phase extraction studies. A satisfactory eluent should effectively elute the sorbed analyte with small volume, which is needed for a high enrichment factor and should not affect the accurate determination of the analyte and reusability of the solid phase. Fig. 2 shows that the adsorption of manganese (II) at pH < 4 is very low; one can expect that elution may be favored in acidic solution. Therefore, various acidic solutions were used for the desorption of manganese (II). 2 mL of various eluents (0.1 mol L⁻¹ of HNO₃, 1.0 mol L⁻¹ of HNO₃, 0.1 mol L⁻¹ of HCl, 1.0 mol L⁻¹ of HCl, 0.1 mol L⁻¹ of HNO₃ in methanol, 1.0 mol L⁻¹ of HNO₃ in methanol, 0.1 mol L⁻¹ of HNO₃ in ethanol and 1.0 mol L⁻¹ of HNO₃ in ethanol) were studied for desorption of manganese (II). The results were shown in Fig. 3. The solution of 1.0 mol L⁻¹ of HNO₃ in ethanol was chosen for the stripping of the sorbed manganese (II) ions, because it was an efficient solution and also a suitable matrix for the determination of the analyte by FAAS. The effect of the volume of the eluent was also investigated. It was found that 1.0 mL of this reagent was sufficient to elute the retained analyte.

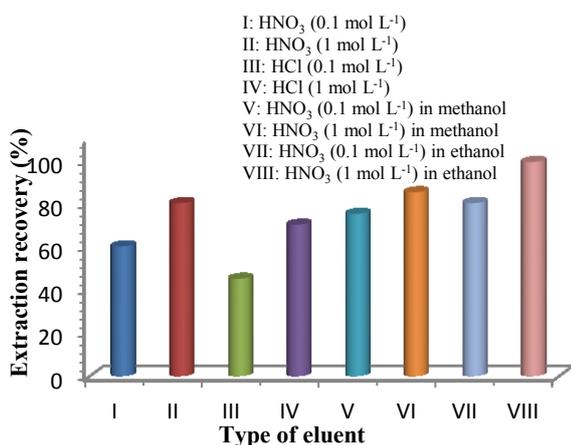


Fig. 3. Choice of eluent. Conditions: sample volume: 25 mL, manganese concentration: $100.0 \mu\text{g L}^{-1}$, amount of modified sorbent: 100 mg, eluent volume 2.0 mL.

3.3 The Effect of the amount of modified nano-alumina

The amount of adsorbent is another important parameter to obtain quantitative recovery. For this reason, the amounts of nano alumina modified with 5-Br-PADAP were optimized. The influence of the adsorbent amount was tested in the range of 10-200 mg. According to the results, quantitative recoveries were obtained when nano-sized adsorbent amount was above 30 mg (Fig. 4). Hence, 100 mg of the modified nanometer-sized alumina was used for further experiments owing to the greater availability of the exchangeable sites or surface area at high amounts of the adsorbent and to be used for other extractable species affecting selectivity.

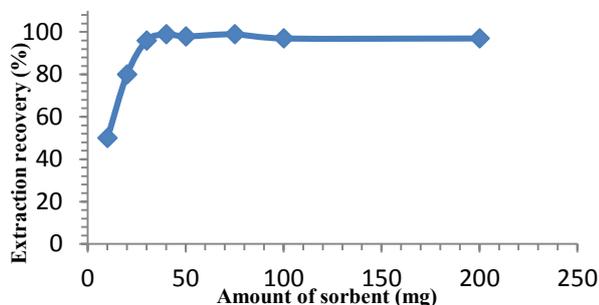


Fig. 4. Effect of the amount of modified nano alumina. Conditions: sample volume: 25 mL, manganese concentration: $100.0 \mu\text{g L}^{-1}$, eluent: 1.0 mL of 1.0 mol L^{-1} of HNO_3 in ethanol.

3.4 The Effect of the sample volume

Due to the low concentrations of trace metals in real samples, the analytes should be taken into smaller volumes for high preconcentration factor by using sample solutions with large volumes. Therefore, the maximum applicable sample volume was determined by increasing the dilution of manganese (II) ions solution, while keeping the total amount of loaded manganese (II) ions fixed ($2.5 \mu\text{g}$). Different feed volumes varied between 10 and 50 mL. It should be noted that owing to limitation for centrifugation of volumes higher than 50 mL, higher volumes of the sample were not investigated. The recoveries were found to be stable until 25 mL and

were chosen as the largest sample volume to work. At volumes higher than 25 mL probably the manganese (II) ions were not sorbed effectively because of the low amount of adsorbent in those volumes. In this study, the final solution volume to be measured by FAAS was 1.0 mL; therefore a preconcentration factor of 25 was obtained from the 25 mL sample.

3.5 The Effect of equilibrium time

The efficiency of the analyte deposition depends on the contact time of the sample with the solid phase. It is necessary to require the preconcentrate of analyte in short time. For this reason, a series of extraction experiments at different shaking time (1, 2, 5, 8, 10, 15, 20, 30 min) were carried out. The results showed that the shaking time (from 1 to 30 min) has no effect on the extraction efficiency of manganese (II) and the extraction was quantitative. Although the extraction process can be continued during the centrifugation, the results showed that extraction was quantitative and very fast in all cases. Thus, the mixtures have been shaken for 1 min to reach equilibrium in the subsequent experiments.

3.6 Adsorption capacity

The capacity of the sorbent is an important factor which determines how much sorbent is required to remove specific amounts of metal ions from the solution, quantitatively [38]. To determine the adsorption capacity of the modified adsorbent, a batch method was selected. A 25 mL aqueous solution containing different amounts of manganese (II) ions at pH 10.0 were added to 100 mg of modified nano alumina. After shaking for 30 min, the solid phase was separated by centrifugation and the concentration of manganese ion was determined in the supernatant solution by FAAS. The capacity of the modified adsorbent for manganese (II) ions was found to be 18.5 mg g^{-1} .

3.7 The Effect of ionic strength

The influence of ionic strength on the extraction of manganese (II) was studied in the sodium chloride solution with various concentrations ranging from 0.0 to 2.0 mol L^{-1} . The results indicated that ionic strength has no significant effect on extraction efficiency up to 2.0 mol L^{-1} of NaCl. These observations showed the specific tendency of modified nano alumina for manganese (II) ions and the possibility of using this method for the separation of manganese (II) from the solution with high ionic strength.

3.8 The Effect of foreign ions

To assess the possible analytical applications of the recommended procedure, the effect of some foreign ions which interfere with the determination of manganese (II) ion was examined with the optimized conditions. For these studies, a fixed amount of metal ion ($100 \mu\text{g L}^{-1}$) was taken with different amounts of foreign ions and the recommended procedure was followed. Tolerable limit was defined as the highest

amount of foreign ions that produced an error not exceeding 5% in the determination of manganese (II). The results are summarized in Table 1. As can be seen, the large numbers of ions used have no considerable effect on the extraction and determination of manganese (II) ions.

Table 1. Effect of foreign ions on the recovery of manganese (100.0 $\mu\text{g L}^{-1}$)

Ion	Ion/Mn (II) ratio (w/w)	Recovery (%)
F ⁻	10000	98
Cl ⁻	10000	99
Br ⁻	10000	98
I ⁻	10000	97
ClO ₄ ⁻	10000	98
HCO ₃ ⁻	10000	97
SO ₄ ²⁻	10000	100
PO ₄ ³⁻	10000	98
Li ⁺	10000	100
K ⁺	10000	99
Ba ²⁺	10000	99
Mg ²⁺	10000	99
Ca ²⁺	10000	98/
Zn ²⁺	1000	98
Cd ²⁺	1000	97
Cr ³⁺	1000	98
Ag ⁺	500	97
Pb ²⁺	500	98
Al ³⁺	500	99
Ni ²⁺	500	97
Cu ²⁺	500	97
Fe ²⁺	500	98
Fe ³⁺	500	97

3.9. Method validation

Under the optimum experimental conditions, the limit of detection (LOD), defined as $3S_b/m$ (where S_b and m

are the standard deviation of the blank and the slope of the calibration graph, respectively), was found to be $0.9 \mu\text{g L}^{-1}$. The relative standard deviation (RSD) for 10 replicate measurements of $100 \mu\text{g L}^{-1}$ manganese (II) was 2.2%. The calibration graph was linear in the range of $5\text{--}160 \mu\text{g L}^{-1}$ of manganese (II) in the initial solution and obeyed the equation $A = 0.005 C + 0.0132$ ($r^2 = 0.9986$), where A is the absorbance and C is the concentration of manganese (II) ($\mu\text{g L}^{-1}$). The preconcentration factor that was calculated by dividing the sample solution volume into the eluent volume was 25.

3.10. Analysis of natural water and milk samples

In order to test the reliability of the proposed methodology, it was applied to the determination of manganese (II) in several natural water and milk samples. Real water samples (tap water, mineral water, river water, and sea water) and milk samples were subjected to the proposed method to evaluate the concentration of manganese. The obtained results are shown in Table 2. Recovery studies were also carried out after known manganese (II) concentrations were spiked to samples at levels of 50 and $100 \mu\text{g L}^{-1}$. The recovery values calculated for the added standards ranged from 97 to 102 %. These results confirm the accuracy of the procedure and its independence from the matrix effects.

3.11. Comparison with other methods

A comparison of the presented method with other reported preconcentration methods for manganese determination is given in Table 3. The presented method has low LOD, good enrichment factor and good RSD and these characteristics are comparable or even better than most of the other methods named in Table 3. All these results indicate that presented is a reproducible, simple, and low cost technique that can be used for the preconcentration and determination of manganese (II) in real samples.

Table 2. Determination of manganese (II) in food and water samples

Sample	Mn (II) amount ($\mu\text{g L}^{-1}$)		Recovery (%)
	Added	Found ^a	
Cow Milk (Local supermarket, Sari, Iran)	0.0	18.4 ± 0.5	–
	50.0	67.3 ± 1.6	97.8
	100.0	117.2 ± 2.7	98.8
Tap water (Drinking water system of Behshahr, Iran)	0.0	n.d. ^b	–
	50.0	49.1 ± 0.9	98.2
	100.0	97.1 ± 2.3	97.1
Mineral water (Damavand mineral water, Iran)	0.0	n.d.	–
	50.0	51.1 ± 0.8	102.2
	100.0	101.6 ± 2.4	101.6
River water (Gorgan river, Gorgan, Iran)	0.0	16.5 ± 0.6	–
	50.0	66.2 ± 1.8	99.4
	100.0	117.4 ± 2.9	100.9
Sea water (Caspian sea water, Bandar Torkaman, Iran)	0.0	5.2 ± 0.2	–
	50.0	55.6 ± 1.8	100.8
	100.0	104.8 ± 2.6	99.6

^a Mean \pm standard deviation ($n = 3$)

^b Not detected

Table 3. Comparison of the present method with other pre-concentration methods for determination of manganese (II)

Method	LOD ^a ($\mu\text{g L}^{-1}$)	RSD ^b (%)	PF ^c	Reference
CPE-FAAS	5	–	20	[12]
SPE-FAAS	1.0	3.5	33	[39]
SPE-FAAS	0.7	4.5	17	[40]
CPE-FAAS	1.4	4.3	20	[41]
CPE-FAAS	2.9	1.3	17	[42]
DLLME-	4.0	3.8	5.9	[43]
UV-Vis				
USAEME- FAAS	0.5	2.9	12.5	[44]
SPE -FAAS	0.9	2.2	25	Present work

^a Limit of detection^b Relative standard deviation^c Preconcentration factor

4. CONCLUSION

The preparation of a new sorbent through the modification of nano alumina with SDS and 5-Br-PADAP has been described and shown to be an alternative and efficient route for separation and preconcentration in the determination of manganese (II). The method is simple, rapid and economical. This sorbent has fast adsorption and desorption kinetics. This methodology displays good accuracy, low limit of detection, excellent precision, which in turn show its potentiality in trace analysis of various samples with complicated matrix.

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