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pH-controlled solid-phase enrichment of Mn(II): confirmation of the structure of the extracted ternary Mn(II) complex by single crystal X-ray structure analysis

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ABSTRACT

Trace-level (μg g^{-1}) selective separation of Mn(II) from other associated metal ions have been carried out by impregnating equimolar mixture of pyridine-2, 6-dimethanol (PDM) and thiocyanate ion on silica. The sorbent showed maximum Mn(II) sorption capacity (1.23 mmol g^{-1}) at pH 5.0. Mn(II) was completely eluted by 8.5 mL 1.0 mol L^{-1} HNO_3 from 1.0 g sorbent and subsequently measured with flame atomic absorption spectrometer (FAAS).The structure of the extracted Mn(II) complex was established by Fourier transform infrared red spectra and confirmed by single crystal X-ray structure analysis. Thermogravimetric analysis (TGA) shows the stability of the isolated Mn(II) complex at the extraction temperature. Three sigma detection limit ($N = 10$) of the method was 0.6 μg mL^{-1} with a relative standard deviation of 0.1% ($N = 10$). The method has a pre-concentration factor of 105. Marginal interference from Cu^{2+} has been masked with NH_4SCN. The developed method has been tested for trace-level separation and estimation of Mn(II) in spiked water samples.

Keywords: Mn(II); Pyridine 2,6-dimethanol; Thiocyanate; pH; Crystal structure; Flame atomic absorption spectroscopy

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1. Introduction

Manganese is the 11th abundant element on the earth crust. Though it is essential trace element for human beings [1,2] but consumption in excess quantity may be fatal to human beings [3]. It is also present in several enzymes like, hydrolase, decarboxylase, and transferase enzyme and plays a key role in the synthesis of glycoprotein and proteoglycans [4]. Therefore, pre-concentration and trace-level estimation of manganese is a challenging area in analytical chemistry.

Direct determination of Mn(II) in environmental samples by conventional spectro-analytical techniques like flame atomic absorption spectrometry (FAAS) and inductively coupled plasma optical emission spectrometry is difficult because of matrix interference and low analyte concentration below the detection limit [5]. Consequently, several pre-concentration/separation methods like solvent extraction, co-precipitation, ion exchange, and solid-phase extraction have been widely used. Amongst them, solid-phase extraction have become very popular and attractive due to its high pre-concentration factor, and easy regeneration of the sorbent for multiple sorption–desorption cycles

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with good reproducibility, simplicity, and automation possibility. Several solid sorbents *viz.* activated carbon [6,7], activated bentonite [8], duolite XAD-761 [9], chromosorb 102 [10], amberlyst 36 [11], and amberlite XAD series [12,13] have been used for enrichment of metal ions from dilute solutions prior to determination by a variety of analytical techniques. Amongst them, silica immobilized with organic chelating compounds has received great interest for its non-swelling properties, large specific surface area, fast kinetics, good mechanical, thermal and chemical stability [14,15]. Till date, there are only few reports on trace-level separation of Mn(II) using chelating ligands immobilized on solid support [16–19]. None of them has established the structure of the extracted Mn(II) complex by single crystal X-ray structural analysis which nowadays provide the most powerful and authenticated method to prove the binding of the ligand with metal ion. Herein, we report, trace-level recovery of Mn(II) by chelation assisted SPE with pyridine-2, 6-dimethanol (PDM) and thiocyanate. Mn(II) binding by the ligand had been confirmed by single crystal X-ray structural analysis of the extracted Mn (II) complex. The developed method was verified by analyzing certified reference materials and applied to the analysis of environmental samples and alloys. Different analytical figures of merit were also reported.

2. Experimental

2.1. Instrumentation

A VARIAN (Spectra AA 55) flame atomic absorption spectrophotometer (FAAS) (Australia) was used for measuring concentration of Mn(II). All measurements were performed using integrated absorbance. Hollow cathode lamp for Mn was operated at 9.0 mA and at wave length of 279.5 nm with a slit width of 0.2 nm. D_2-back ground correction was performed in all the measurements. Air and acetylene flow rates were maintained at 10 and 2 L min^{-1}, respectively. Fourier transform infrared red (FTIR) spectra were recorded on a JASCO FTIR spectrophotometer (model: FTIR-H20). Thermo gravimetric analysis (TGA) was done on a Perkin–Elmer Thermo gravimetric analysis lab system 1 (Technology by SII). pH measurements were performed with a Systronics digital pH meter (model 335). A domestic Samsung microwave oven (model CE2933) with a 2,450 MHz frequency magnetron and 900 W maximum power and a polytetrafluoroethylene reactor (115 mL internal volume, 1 cm cell wall thickness and hermetic screw caps) was used for digestion. Extraction temperature was monitored by using biochemical oxygen demand (BOD) incubator (YONA, India). The X-ray crystal data were collected at 93 K by using a Rigaku MM007 High brilliance RA generator/confocal optics and Mercury CCD system. Intensities were corrected for Lorentz polarization and absorption. The structures were solved by direct methods. Hydrogen atoms bound to carbon were idealized. Structural refinements were obtained with full-matrix least-squares based on F^2 using the program SHELXTL [20].

2.2. Chemicals and reagents

A stock solution of Mn(II) having concentration of 1,000 $\mu\text{g mL}^{-1}$ was prepared by dissolving appropriate quantity of Mn(II) chloride tetrahydrate (Merck, India) in deionized water. A working solution containing 50 $\mu\text{g mL}^{-1}$ Mn(II) was prepared by appropriate dilution. Potassium periodate (Merck, India) was used as received. Spectroscopic grade potassium bromide (SRL, India) was used for making pellets for FTIR studies. PDM (Aldrich, USA), ammonium thiocyanate and silica (80–120 mesh, SRL, India) were used as received. Deionized water from a Milli-Q Millipore® 18.2 M cm resistivity purification system (Bedford, MA, USA) was used to prepare all solutions. Buffer solutions of pH 2–3 and pH 4–6 were prepared by mixing appropriate ratios of H_3PO_4 with KH_2PO_4, citric acid with potassium citrate and acetic acid with sodium acetate, respectively [21,22]. All other chemicals and reagents used were of analytical reagent (AR) grade.

2.3. Preparation of column

The impregnation of PDM and NH_4SCN was done by mixing them in appropriate quantities (1:1, mole/mole) in methanol with silica beads. The mixture was then stirred till the solvent evaporated. The modified silica beads (sorbent) thus obtained were kept overnight at ambient temperature.

2.4. General procedure

Sorption and desorption studies were carried out both by batch and column method. Air-dried sorbent (1.0 g) was either taken in a standard joint conical flask (100 mL) or packed in a glass column (100 mm × 10 mm) and was allowed to be in contact with the sorbent. For column method, both sorption and desorption characteristics for Mn(II) were studied at the optimum flow rate. The sorbent (bed, in case of column) was thoroughly washed with 0.1 mol L^{-1} HNO_3 followed by deionized water till the effluent was free from acid. A sample solution containing 50 $\mu\text{g mL}^{-1}$ Mn(II) was passed through the column.

Any adhering metal ions (not sorbed) were completely washed out by using solutions of appropriate pH. Sorbed Mn(II) (1.0 g) was completely eluted with suitable eluent. Eluted Mn(II) was measured by FAAS. Different experimental parameters such as sample volume, flow rate, pH, equilibration time, effect of foreign ions, varying nature, and concentration of eluents were studied to optimize the sorption and desorption conditions for Mn(II). Effect of temperature (30–60˚C) on the sorption of Mn(II) by the sorbent was monitored by batch method. The sorbent (0.1 g) was taken in a 100 mL standard joint conical flask and appropriate amount of Mn(II) solution was added to the sorbent at optimum pH. Then, it was placed inside the BOD incubator and shaken at the required temperature for optimum period of time. Finally, the conical flask containing sorbent immersed with Mn(II) solution was taken out and filtered through G4 crucible. The amount of Mn(II) in the filtrate as well as in the sorbent (after elution with suitable eluent) was measured by FAAS. To prove that there was no decomposition of the Mn (II) complex at this elevated temperature, thermal stability of the Mn(II) complex was determined covering the temperature range. LOD which is defined as that analyte concentration giving a signal equal to three times standard deviation of blank signal [23] was estimated. Separation of Mn(II) from other accompanying elements (binary mixture) was performed.

2.5. Equilibration time

Mn(II) solution (25 mL, 50 μg mL^{-1}) was mixed with appropriate amount of sorbent (batch method) at optimum pH and allowed to stand for different times *viz*. 1, 3, 5, 7, 9, 12, 15, 18, and 24 h (for different sets). Concentration of Mn(II) in the filtrate as well as after elution from the sorbent was measured by FAAS.

2.6. Kinetic studies

Amount of Mn(II) sorbed by the sorbent under the optimized experimental conditions was monitored at different time intervals using batch technique as described above (Section 2.5). From that data, rate constant for the sorption of Mn(II) on the sorbent was calculated.

2.7. Effect of foreign ions

Several binary synthetic mixtures were prepared and equilibrated with the sorbent at optimum conditions (batch method). In mixtures, foreign ions were taken 200-fold excess to Mn(II).

2.8. Desorption of metal ions

Sorbent (1.0 g) obtained after uptake of Mn(II) ion in the above-mentioned batch technique was shaken with 25 mL of different eluents (1–5.0 mol L^{-1} HNO$_3$, 1–3.0 mol L^{-1} HCl) for 12 h and filtered. The concentration of Mn(II) in the filtrate was measured by FAAS.

2.9. FTIR and single crystal X-ray structural characterization of the extracted complex

Spectroscopic grade KBr (after removal of moisture at 100˚C in hot air oven followed by cooling at room temperature in a desiccator) was mixed with the sample. The mixture was grinded with mortar and pestle to make very fine powder. A semitransparent pellet was prepared with that powder using a hydraulic

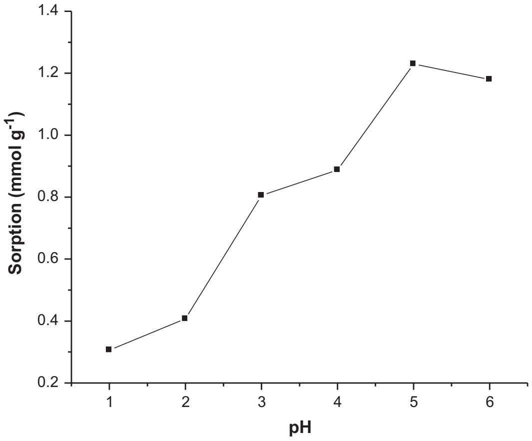

Fig. 1. Equilibrium sorption of Mn(II) (mmol g^{-1}) by the sorbent as a function of pH.

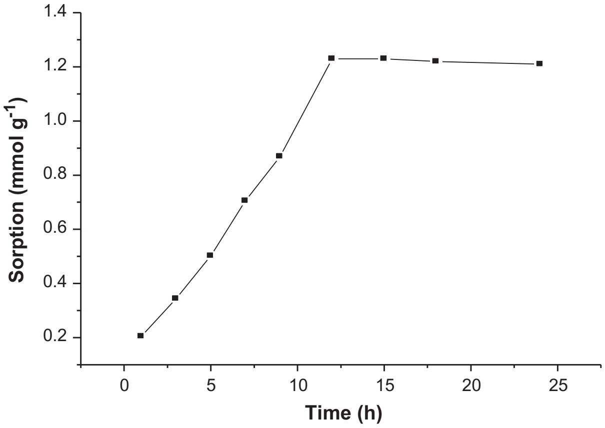

Fig. 2. Equilibrium sorption of Mn(II) (mmol g^{-1}) by the sorbent as a function of time.

system. The pellet was then placed in the FTIR instrument to record the FTIR spectrum.

Single crystals of the extracted Mn(II) complex were grown from the methanol solution obtained after elution of Mn(II) from the sorbed material by slow evaporation technique. After one week, pale pink crystals were formed. Pale pink color crystals were collected and mounted on the diffractometer. Data collected were refined as described in the *instrumentation* section.

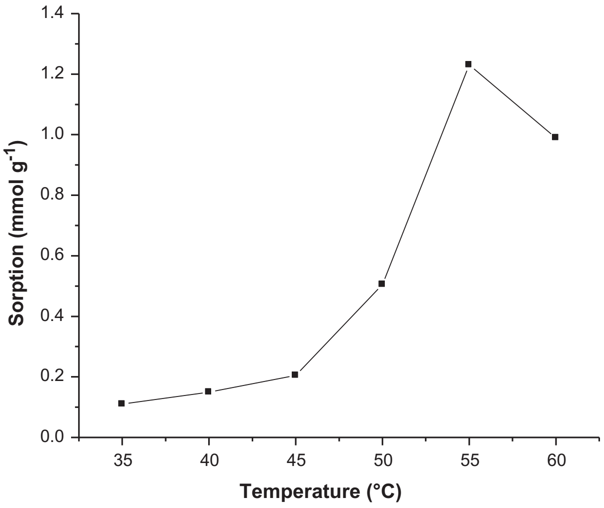

Fig. 3. Equilibrium sorption of Mn(II) (mmol g^{-1}) by the sorbent as a function of temperature.

3. Results and discussion

3.1. Sorption studies

Fig. 1 indicates that with increasing pH, sorption of Mn(II) gradually increases to a level of pH 5.0. Decrease in sorption capacity at higher acidity may be attributed to the protonation of donor sites. Hence, pH 5.0 is preferred throughout the entire study. Fig. 2 clearly shows that with increasing time, sorption capacity increases, and after 12 h, no further change in sorption capacity has been observed. Fig. 3 demonstrates that sorption of Mn(II) gradually increases with temperature, to a maximum value at 55°C. No decomposition of the Mn(II) complex is observed at this elevated temperature (Fig. 4).

The sample flow rate should be optimized to ensure quantitative retention along with minimization of the time required for sample processing. From Fig. 5, it is found that with increasing flow rate from 0.5 to 1.5 mL min^{-1}, the recoveries of manganese remains unchanged up to 1.5 mL min^{-1}, after which it decreases. Hence, sample flow rate of 1.5 mL min^{-1} is selected.

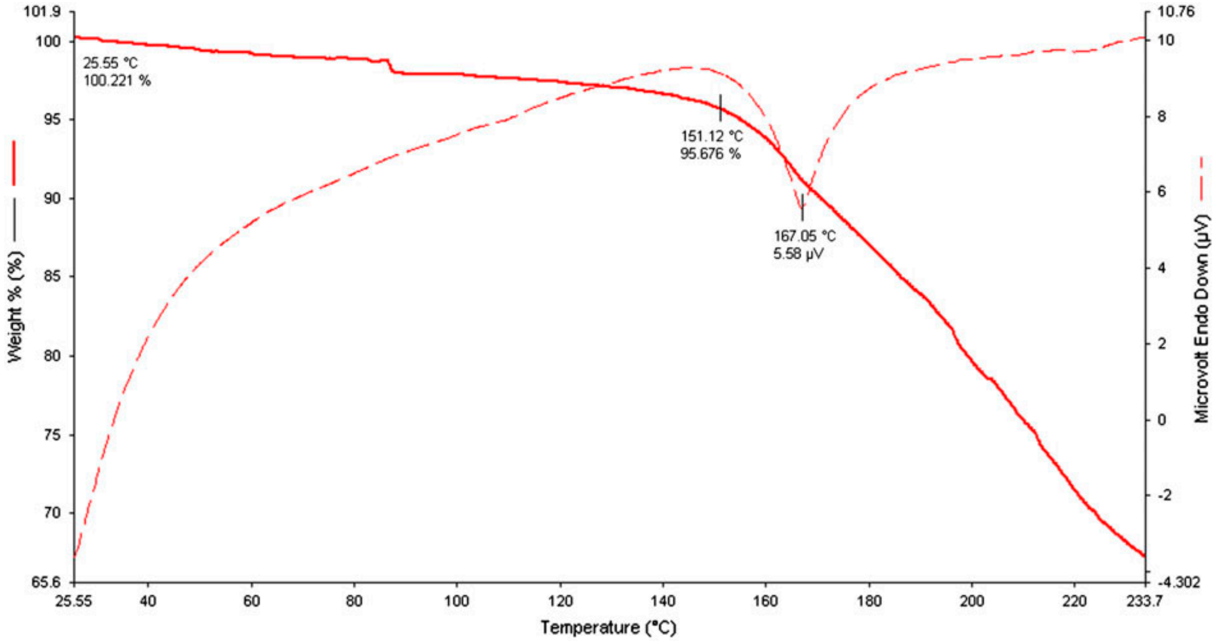

Fig. 4. TGA/DTG of the Mn(II) complex.

Fig. 6 reveals that the percentage of sorption drops after passing 900 mL of Mn(II) solutions through the sorbent which may be due to the saturation of the sorbent with Mn(II).

The rate of exchange of metal ion by a sorbent has been controlled by a second-order kinetic equation [24]. Using the equation $\ln Z = 2kQ_0(Q_0 - Q_\alpha)t/Q_\alpha$, where $Z = [Q_t(Q_0 - 2Q_\alpha) + Q_0Q_\alpha]/Q_0(Q_\alpha - Q_t)$ developed by Turse and Riemen [25], the rate constant k was calculated from the slope, S of the equation: $S = 2kQ_0(Q_0 - Q_\alpha)/Q_\alpha$, where Q_t is the amount (mmol) of Mn(II) exchanged at time t, Q_α, is the maximum sorption capacity (mmol) at equilibrium and Q_0 is the amount (mmol) of sorbent, in terms of milimoles of Na^+ exchanged after 24 h. The observed values of Q_α and Q_0 are 1.23 and 2.9 mmol g^{-1}, respectively. A plot of ln Z vs. t is linear passing through zero. Fig. 7 provides the values for slope (S) and rate constant (k) as 0.132 and 0.0167 mmol^{-1} min^{-1}, respectively.

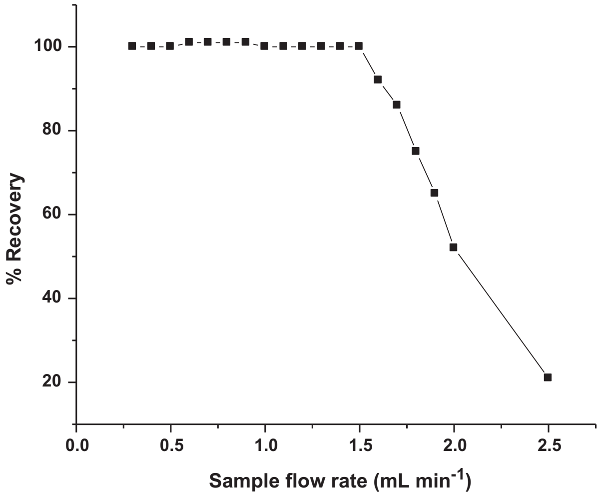

Fig. 5. Effect of sample flow rate (mL min^{-1}) on the recovery of Mn(II) at optimum conditions.

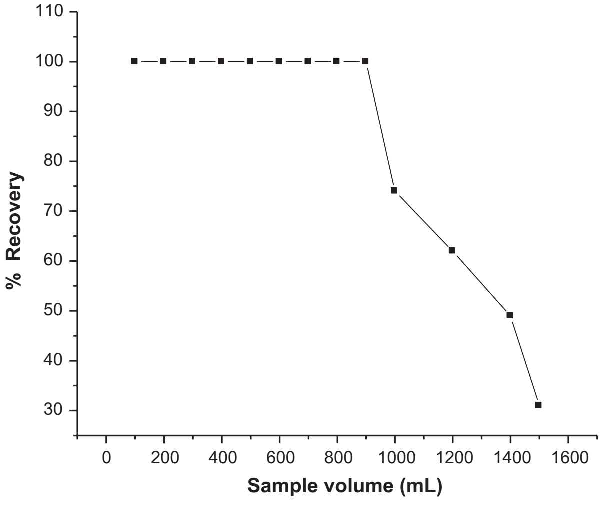

Fig. 6. Sample breakthrough volume for the sorption of Mn(II) at optimum conditions.

In the presence of 200-fold excess of diverse metal ions (binary mixtures) like alkali, alkaline earth, and transition metal ions, more than 90% recovery for Mn (II) have been observed. Insignificant interference from Cu(II) have been eliminated by masking it with NH_4SCN. Amongst various anions, VO_3^- interferes to some extent. The results are presented in Table 1. Extraction recovery could be represented by the equation:

$$E = (\%) = (C_0 - C_\alpha)/C_0 \times 100 \tag{1}$$

where E (%) represents the extraction percentage, C_0 and C_α are the initial and equilibrium concentrations of Mn(II). We have found 100.0 ± 0.3% extraction of Mn(II) at the optimized conditions.

3.2. Elution studies

Quantitative recovery of Mn(II) from the sorbed material was necessary for repeated use of the sorbent. Table 2 shows the efficiency of different eluents for the recovery of Mn(II) from the sorbent. Recovery of Mn(II) is 100.0 ± 0.3% with 1 mol L^{-1} HNO_3. The effect of eluent volume for quantitative recovery of Mn(II) has been investigated separately. It is found that 8.5 mL HNO_3 (1.0 mol L^{-1}) is very useful for quantitative recovery from 1.0 g sorbent (Fig. 8). The effect of elution flow rate (Fig. 9) on the recovery of Mn(II) have been investigated. At a

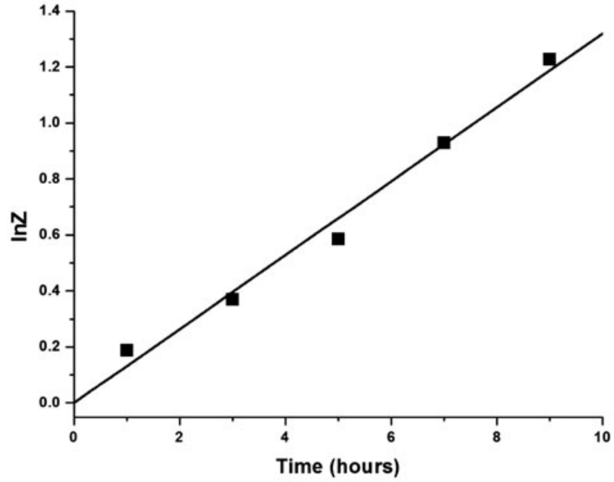

Fig. 7. Second-order plot for the sorption of Mn(II).

Table 1
Effect of foreign ions (in a binary mixture) on the sorption of Mn(II)

Foreign ions*	% recovery of Mn(II)	Foreign ions*	% recovery of Mn(II)
Ag(I)	99.5	Fe(III)	99.9
Cu(II)	94.3	Na(I)	99.7
Hg(II)	99.4	Cl^-	98.2
Zn(II)	101.4	AsO_4^{3-}	100.4
Mg(II)	97.9	VO_3^-	97.4
Ni(II)	99.8	PO_4^{3-}	100.4
Co(II)	98.8	CrO_4^{2-}	98.9
Cr(III)	97.2	MnO_4^-	99.4
Ca(II)	99.6		

*Coexisting ions are 200 fold to [Mn(II)].

Table 2
Effect of eluents on the recovery of sorbed Mn(II) on PDM-SCN loaded silica

Eluents ($mol\,L^{-1}$)	% Recovery[a]	Eluents ($mol\,L^{-1}$)	% Recovery[a]
HCl (1)	36 ± 0.8	HNO_3 (0.1)	23 ± 0.2
HCl (2)	41 ± 0.6	HNO_3 (0.5)	49 ± 0.4
HCl (3)	50 ± 0.3	HNO_3 (1)	100 ± 0.3
HCl (4)	61 ± 0.9	HNO_3 (2)	100 ± 0.5
		HNO_3 (3)	101 ± 0.5

[a] Average of three replicate measurements ± % RSD.

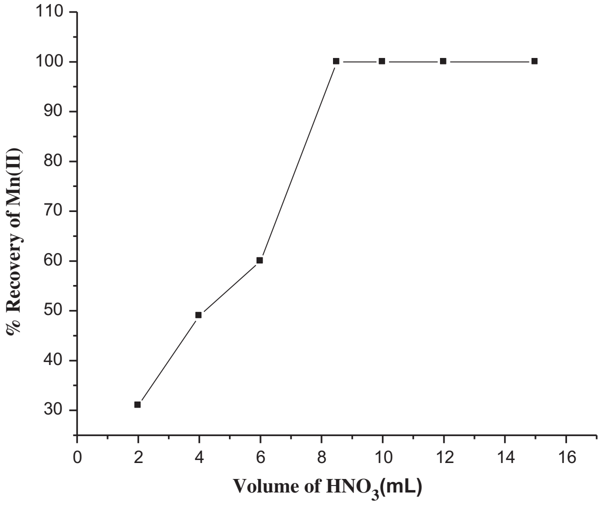

Fig. 8. Desorption of Mn(II) as a function of volume of the eluant.

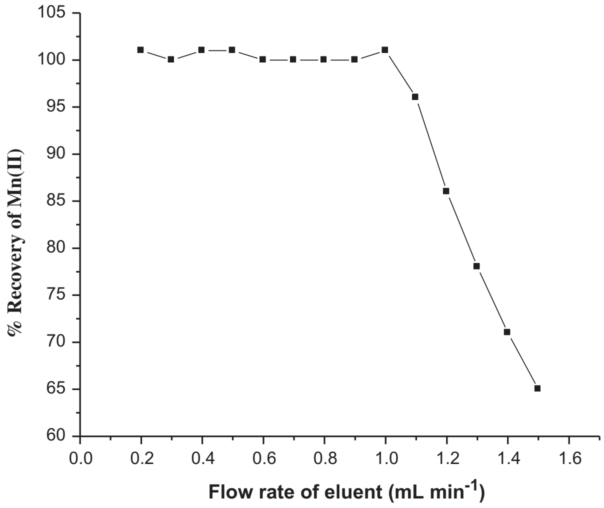

Fig. 9. Effect flow rate of the eluent on the recovery of Mn (II).

flow rate range of 0.2–1.0 $mL\,min^{-1}$, 100.0 ± 0.3% recovery of Mn(II) has been observed. Consequently, elution flow rate of 1.0 $mL\,min^{-1}$ is maintained.

3.3. FTIR and single crystal X-ray structural confirmation of the extracted Mn(II) complex

FTIR spectra of the PDM-loaded silica (Fig. 10) has been compared to that of the Mn(II) complex loaded on silica (Fig. 11). The O–H band of the free PDM ligand at 3360.81 cm^{-1} has been red shifted to 3067.66 cm^{-1} in the Mn(II) complex, indicating the "O" donor site of PDM is involved in Mn(II) binding. Appearance of a new sharp band at 2078 cm^{-1} has been assigned unambiguously to thiocyanate stretching [26]. Appearance of a new pair of sharp bands at 1533.31 and 1431.92 cm^{-1} has been assigned to C=O and C–O stretching frequencies for acetate moiety. Similarly, other characteristics frequencies of the free PDM ligand have also been shifted. Selected stretching frequencies have been presented in Table 3. More powerful evidence of the Mn(II) binding ability of PDM/ SCN^- is provided by the single crystal X-ray structure of the Mn(II) complex (Fig. 12). Crystal data and structure refinement for the Mn(II) complex are presented in Table 4. Detailed bond lengths and bond angles of the complex have been presented in Table 5. Fig. 12 clearly shows that two PDM units bind differently to Mn(II). One PDM unit acts as a monodentate O-donor while the other PDM behaves as a tridentate ONO donor. In both cases, no deprotonation of hydroxymethyl groups have occurred to the O-donor. Mn(II) is hexa-coordinated (MnN_2O_4 chromophore) with one acetate ion from the acetate buffer (used to

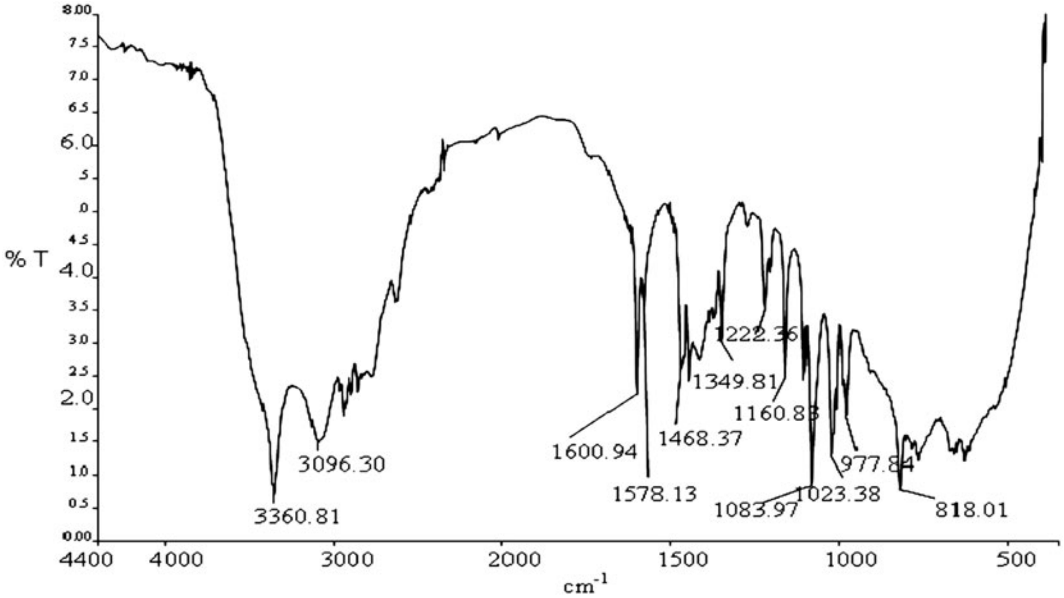

Fig. 10. FTIR spectrum of the immobilized pyridine 2, 6-dimethanol on silica.

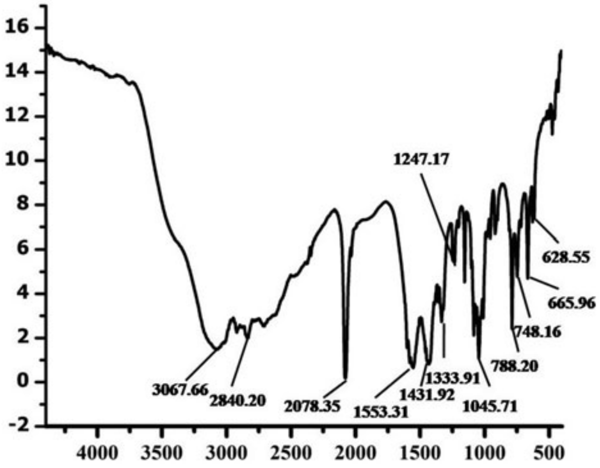

Fig. 11. FTIR spectrum of the immobilized Mn(II) complex on silica.

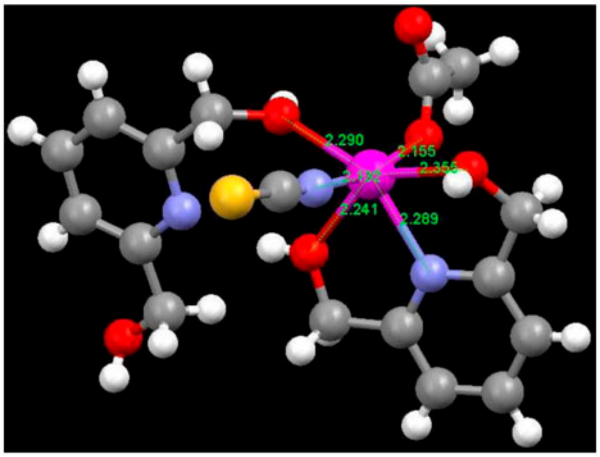

Fig. 12. Single crystal X-ray structure of the extracted Mn (II) chelate complex. Selected bond lengths are indicated close to the respective bonds.

Table 3
Comparison of FTIR data of free PDM with its Mn(II) complex

	$\nu_{O\text{–}H}$ (cm^{-1})	ν_{SCN} (cm^{-1})	ν_{CH_3COO} (cm^{-1})
Free PDM ligand	3360.81	—	—
Mn(II) complex	3067.66	2078	1533.31, 1431.92

Table 4
X-ray structural parameters of the isolated Mn(II) complex

Space group	P 1
a, Å	9.5957(17)
b, Å	10.354(2)
c, Å	10.895(3)
α, deg	64.479(7)
β, deg	84.778(6)
γ, deg	86.679(6)
V, Å3	973.516

Table 5
Sorption characteristics of the sorbent for Mn(II)

Maximum sorption capacity (pH 5.0)	1.23 mmol g^{-1}
Complete elution	8.5 mL 1.0 mol L^{-1} HNO_3
Detection limit (N = 10)	0.6 μg mL^{-1}
Pre-concentration factor (%)	105
Sample flow rate	1.5 mL min^{-1}
Sample volume (50 μg mL^{-1} Mn(II))	900 mL
Elution flow rate	1.0 mL min^{-1}
Equilibrium time	12.0 h
Interference [% recovery of Mn(II)]	Cu(II)(94.3%), VO_3^- (97.4%)

maintain the pH of the medium at 5.0 during sorption) coordinates in a monodentate fashion. SCN^- also binds to Mn(II) as an end-on N-donor ligand. Non-bonding of S-site of SCN^- may be explained in terms of HSAB principle. Oxygen being hard donor site, upon binding to Mn(II) increases the hardness of the metal center and hence relatively hard donor site of SCN^- i.e. N-donor site binds to Mn(II). Methanol could also be used to elute Mn(II) complex from the column but methanol unloaded the chelating ligand PDM from the column. So, reloading of the column with PDM was necessary. So, choice of methanol as eluting agent was rejected. Chelated Mn(II) complex was an inner metallic complex of the first order (both charge and coordination numbers are satisfied by the PDM and SCN^- ligand) and insoluble in aqueous solution and remains stacked on the silica column.

4. Analytical performance

The pre-concentration factor is one of the most important parameters to evaluate the performance of solid-phase extraction methodologies. It is the ratio of sample volume to the volume of eluent used for quantitative recovery (100.0 ± 0.3%) of Mn(II). A pre-concentration factor of 105 (900/8.5) could be achieved using the present method. The optimum conditions for maximum sorption of Mn(II) by the present method are shown in Table 5. The sorption characteristics of the present method have been compared with other Mn(II) sorbents available in the literature (Table 6) [16–19].

5. Application

Spiked water samples have been analyzed and a fair degree of recovery of Mn(II) is observed (Table 7).

Table 7
Recoveries of Mn(II) from spiked sample solutions

No.	Amount of Mn(II) added (μg g^{-1})	Amount of Mn(II) found (μg g^{-1})
1	20	19.2 ± 1.8
2	25	23.8 ± 1.2
3	30	30.4 ± 0.4
4	15	16.1 ± 1.1
5	10	9.7 ± 0.3

Table 6
Comparison of the present method for separation of Mn(II) with other SPE methods based on silica or alumina

Matrix	Capacity	LOD (μg mL^{-1})	Eluent	Pre-concentration factor	Samples analyzed
4-(2-pyridylazo)resorcinol [16]	—	0.1	0.5 mol L^{-1} HCl	—	Brackish lake water samples
2-(2-quinolinylazo)-5-diethylaminophenol [17]	—	0.002	Methanol (containing 0.2% of acetic acid and 0.1% of CTMAB)	100	Drinking water
Ambersorb 572 [18]	0.00013 (mg g^{-1})	0.68	1 mol L^{-1} HNO_3	100	Tap water, river water
3% (w/w) 1-(2-pyridylazo)-2-naphthol (PAN) [19]	—	0.5	10 mol L^{-1} DMF	20	Water samples
Pyridine 2,6-dimethanol and thiocyanate (1:1, mole ratio) impregnated on silica [present method]	1.23 (mmol g^{-1})	0.6	1 mol L^{-1} HNO_3	105	Spiked water samples

6. Conclusion

Mixture of PDM and SCN^- immobilized on silica could efficiently remove and pre-concentrate trace-level Mn(II) at pH 5.0. The method is very simple, fast, and selective. PDM has hard donor sites like "O", and border line donor sites like pyridine -N, which bind border line Mn(II) to form water insoluble inner metallic complex in presence of SCN^-. SCN^- contains both soft and border line donor sites, like S and N to coordinate Mn(II). The binding of the reagents (PDM and SCN^-) to Mn(II) has been confirmed by single crystal X-ray structure analysis of the isolated Mn(II) complex and corroborated from FTIR spectroscopy. Finally, the proposed method has been used for selective recovery of Mn(II) from spiked water samples. The sorbent provided high pre-concentration factor (105), reusability (at least 10 cycles), and good LOD ($0.6\,\mu g\,mL^{-1}$).

Symbols and abbreviations

a, Å — crystallographic distance along "x" axis, in a unit cell, degree angstrom.
A.R. — analytical reagent
b, Å — crystallographic distance along "y" axis, in a unit cell, degree angstrom.
c, Å — crystallographic distance along "z" axis, in a unit cell, degree angstrom.
F W — formulae weight
PDM — pyridine-2,6-dimethanol
RSD — relative standard deviation
SPE — solid phase extraction
V, Å^3 — volume, cubic degree angstrom
Z — no. of molecules present per unit cell
α, deg — crystallographic angle in a unit cell between b and c, degree
β, deg — crystallographic angle in a unit cell between c and a, degree
γ, deg — crystallographic angle in a unit cell between a and b, degree

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