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An Extractive pH Dependent Solid Phase Spectrophotometric (SPS) Determination of Mn (II) and Cu (II) by using N, N'-bis(5-(4-nitrophenyl)diazenyl)-2-hydroxybenzylideneamino) Ethylenediimine (NDHBDED) Modified with Alumina

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ABSTRACT

A new azo dye Schiff base ligand, namely 1, 1'-bis(5-(4-nitrophenyl)diazenyl)-2-hydroxybenzylideneamino) ethylenediimine (NDHBDED) has been synthesized and it was impregnated with alumina for extractive determination of metal ions. In this report the sorbent matrix was used for extractive determination of Mn (II) and Cu (II) ions by solid phase spectrophotometric (SPS) method. Both the metal ions were extracted at pH 6.5 and 5.5 respectively. The complexes show maximum absorbance at λ_{max} 590 nm and 570 nm respectively for Mn (II) and Cu (II) ions. The Beer's law range was 10-100 µg/ ml for both the metal ions. Job's method and mole-ratio method showed that metal-ligand ratio in the complexes to be 1:1. The Molar absorptivity for Mn (II) and Cu (II) were 2.351×10^{-4} L mol^{-1} cm^{-1} and 2.225×10^{-4} L mol^{-1} cm^{-1} respectively. The Sandell's sensitivity was 0.004 µg/ cm^2 and 0.008 µg/ cm^2 for Mn (II) and Cu (II) ions respectively. The proposed method was successfully applied to the determination of each metal ion in real samples and tap water.

Key words: Azo dye Schiff base ligand, Mn (II) and Cu (II) complexes, Solid phase spectrophotometric (SPS).

INTRODUCTION

First transition series metals have wide spectrum of industrial applications, especially in steel, catalyst, alloy, electroplating, ceramics & petrochemical industries[1-3]. Some of them play important roles in the biology of micro-organisms, plants and human nutrient. Among heavy elements, Mn (II) and Cu (II) metal ions are problematic in human physiology[4-5].

Manganese is widely distributed in earth crust and biological bodies. Though, manganese is one of the essential elements for human health and for other animal's kingdom as well as for plants[6-9]. Manganese plays an important role across the life span of all mammals. The role of manganese, as a required co-factor for enzymes and basically, in arginase, which is responsible for urea production in the lever, for superoxide dismutase, which is very important antioxidant enzyme. But its higher level is toxic for human health. It affects the central nervous system. Manganase not only affects the ecosystem, but it also causes erosion of household utensils, bath accessories, clothes and unpleasant taste in food, drinks[10-14].

Another heavy metal copper is both vital and toxic for many biological systems. Although trace amount of copper is essential for many biological systems, but its higher concentration is an anthropogenic pollution. It plays a key role in

the formation of hemocyanin which is an important respiratory protein. From the standpoint of human health, its role is involved in hemopoiesis and in maintenance of vascular and skeletal integrity and function of the central nervous system. It occurs naturally in most vegetables, meats, and grains. It plays a key role in regulating vital biological processes[15-17].

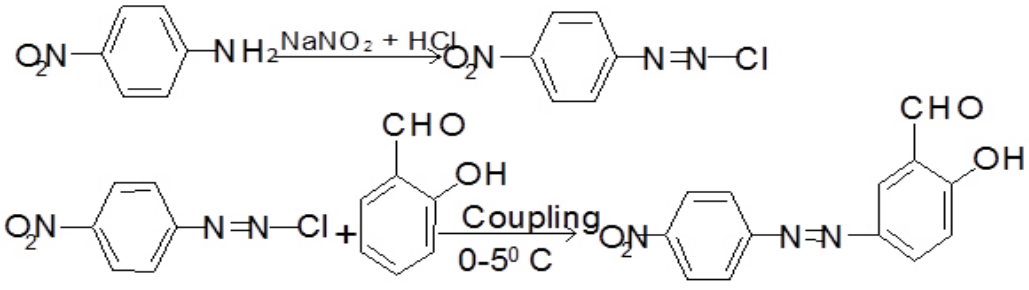
In view from the above standpoints, the separation and determination of Mn ((II) and Cu (II) from different environmental matrices is of great importance. For the determination of both the metal ions at micro level there are several frequently adopted analytical techniques such as electro-thermal atomic absorption spectrometry (ETAAS), AAS, inductively coupled plasma mass spectrometry (ICP-MS), X-ray fluorescence spectrophotometry, spectrofluorometry, and other such technique. Several methods such as liquid-liquid extraction, precipitation, cloud point extraction, co-precipitation and solid phase extraction etc. are used for preconcentration and separation of heavy metals. Out of these above method, the spectrophotometric methods are cheaper and easier to operate and have comparable sensitivity.

A good number of spectrophotometric agents are used for the spectrophotometric determination of the heavy metal ions. These are neutral polymer Amberlite XAD, Amberlite IR-120, activated carbon, octadecyl silica-gel, Dowex IX8, benzophenone, Styrene-divinylbenzene, Pyridine-2,6- dicarboxylic acid, Pyridine-2,6-dimethanol, 2-hydroxy-4-methoxy acetophenone oxime, 4-(2-pyridylazo)resorcinol, malachite green, picolinaldehyde nicotinoyl hydrazone etc[18-25]. But few of them are used for the extraction and determination of the heavy metal ions[26-30]. Azo dye Schiff base ligands are important N_2O_2-donor site containing reagents where some importants heavy metal ions form stable complexes. The metal chelates of these N_2O_2-containing azo dye Schiff base ligands find wide range applications in biological activities and in analytical chemistry. Herein, we introduced a new azo dye Schiff base ligand N, N'-bis(5-(4-nitrophenyl)diazenyl)-2-hydroxybenzylideneamino) ethylenediamine (NDHBDED) for selective solid phase spectrophotometric (SPS) determination of some heavy metal ions from environmental samples. In this report, we impregnated the azo dye Schiff base ligand with alumina for the complexation with Mn (II) and Cu (II) ions prior to solid phase spectrophotometric (SPS) determination of these metal ions.

EXPERIMENTAL

Reagents and Solutions

High purity reagents were of analytical grade from E. Merck, Germany and other metal salts from BDH, India also were of analytical grade reagent. p-nitroaniline, salicyldehyde and ethylenediamine from Sigma and Aldrich were used for the preparation of the ligand and for the complexation. A neutral solid sorbent alumina was used for the determination of metal ions from Oxford Lab., Mumbai, India. Standard stock solutions of Mn (II) and Cu (II) (1mg/ml) were prepared by dissolving appropriate amount of pure grade chemicals in double distilled deionised water with addition of few drops of conc. HCl. The working solutions of metal ions were prepared by diluting appropriate volumes of stock solution with distilled water. The solution of the chelating agent was prepared in ethanol-methanol mixture.



Scheme 1: The reaction scheme of the Azo Coupling of salicyldehyde

Instrumentation

The UV-Vis spectra were recorded in ethanol-methanol mixture using Shimadzu Spectrophotometer (UV-1800). A mechanical shaker (BOD-incubator, YONA Mfg. Indian Instruments Manufacture Co., Kol-12) was used throughout the experiments. A labtronic pH meter (Model No-23) equipped with a combined glass-calomel electrode was used to monitor the pH of the solutions.

Synthesis of Azo dye Schiff base ligand (NDHBDED):

The ligand N, N'-bis(5-(4-nitrophenyl) diazenyl)-2-hydroxybenzylideneamino) ethylenediimine (NDHBDED) was synthesized by our previous reported method.

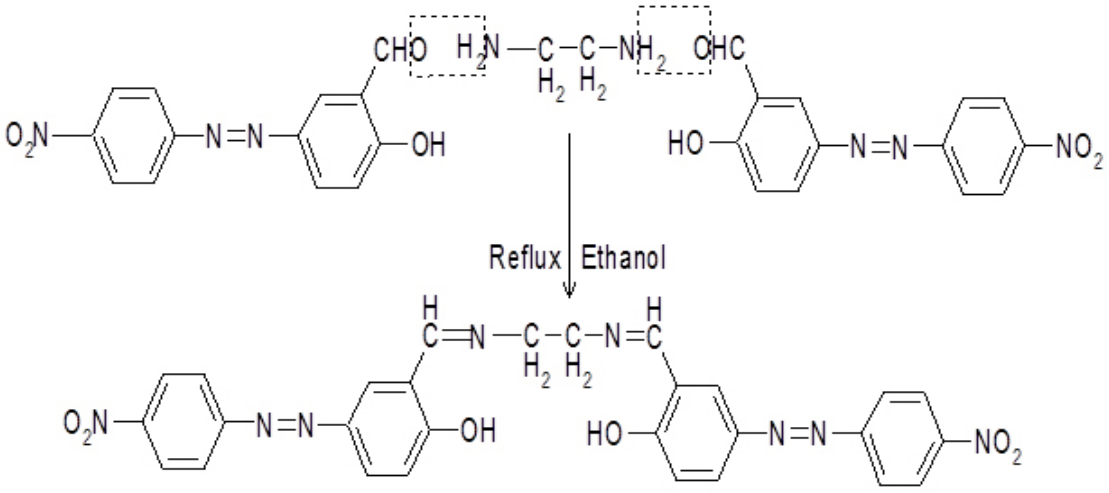
(a) Azo coupling of salicyldehyde

Our proposed diazo compound was synthesized by a reported method. A suspension of p-nitroaniline (2.50 g, 20 mmol) in 30 ml HCl and 10 ml of water was heated from 60-70^0 C until complete dissolution. The clear solution was diazotized with $NaNO_2$ (2.5 g) dissolved in water (10 ml) at 0-5^0 C. The cold diazonium solution was added to a solution of salicyldehyde (4.25 ml, 40 mmol) in 50 ml water containing NaOH (1.5 g) and Na_2CO_3 (10 g) at 0^0 C for 40 minutes. The reaction mixture was stirred during the process. The product was collected and washed with NaCl solution (100ml, 10%). Coupling of the diazonium reagent to the salicyldehyde occurred at the para position to the hydroxyl group. The diazo compound was recrystallized many times from ethyl alcohol and finally dried at 60-70^0 C for at least 3 hours. Yellow solid, yield 91 %, m.p.165-170^0 C, Anal. Calcd. For $C_{13}H_9N_3O_4$; C:57.56, H:3.32, N:15.49, O:23.61%, Found: C:57.60, H:3.31, N:15.45, O:23.6 %. FTIR (KBr cm^{-1}): 1285 (phenolic C-O), 1665 (-CHO group), 1448 (N=N), 1345 (-NO_2 group) cm^{-1} UV-Vis:

λ_{max}=390, 545 nm.

(b) Synthesis of the Azo Dye Schiff Base Ligand (NDHBDED)

For the ligand,N,N'-bis(5-(4-nitrophenyl) diazenyl)-2-hydroxybenzylideneamino) ethylenediimine (NDHBDED), a solution 0.04 mol of previously prepared azo dye and 0.02 mol EDTA in 95 % solution were taken into a 250 ml round bottom flask. Catalytic amount of glacial acetic acid was added to it. The final mixture was allowed to reflux for 3 hours. The product was collected and washed with small amount of ethanol which was soluble in solvents such as ethanol, methanol, DMF and DMSO. The yellow yield was 86 % m.p. 165-170^0 C. Anal. Calcd. $C_{28}H_{22}N_8O_6$, C:59.36, H:3.88, N:19.78, O:16.96 %, Found: C:59.50, H:3.91, N:19.81, O:17.00 %. FTIR (KBr cm^{-1}): 3055 (C-H, aromatic), 2890, 2842 (C-H, aliphatic), 1645 (C=N), 1605 (C=C, aromatic), 1420 (N=N), 1275 (C-O, phenolic) cm^{-1}. UV-Vis: λ_{max}= 275,390,460,545 nm.



N, N'-bis(5-(4-nitrophenyl)diazenyl)-2-hydroxybenzylideneamino)ethylenediimine(NDHBDED)

Scheme 2: The reaction scheme of synthesis of the Azo Dye Schiff Base Ligand

General Procedure

2 g of the azo dye Schiff base (NDHBDED) chelating reagent was impregnated on the surface of 4.0 g of alumina at the ratio 1:2 in ethanol-methanol mixture and stirred for 30 minutes at room temperature. The resulting composition was left in an oven at 60^0 C for 48 hours. After drying, the sorbent was ground into powder for metal ions extraction. For the batch method of extraction 300mg of sorbents were used in each 100 ml flasks with 25 ml of 0.01 (M) solutions of Mn (II) and Cu (II) ions and pH was adjusted to 6.5 using HCl (0.1 M) and NaOH (0.1 M) solutions. The mixture of the sorbent matrix and metal ions solutions were shaken vigorously by a mechanical shaker at room temperature for 30 minutes for adsorption of the metal ions onto the adsorbents.

RESULTS AND DISCUSSION

UV-Vis spectra for NDHBDED shows maximum absorbance at λ_{max} 500 nm, but the spectra of the complexes of Mn (II) - NDHBDED and Cu (II) - NDHBDED give maximum absorbance at λ_{max} 590 nm and 570 nm respectively [Fig. 1 & 2]. N, N'-bis(5-(4-nitrophenyl)diazenyl)-2-hydroxybenzylideneamino) ethylenediimine(NDHBDED) forms coloured complexes with Mn (II) and Cu (II) which are stable and their extraction could be quantitative at pH 6.5.

A series of standard solutions containing Mn (II) and Cu (II) in aqueous solution were taken and calibration curve were constructed by plotting absorbance against the amount of Mn (II) and Cu

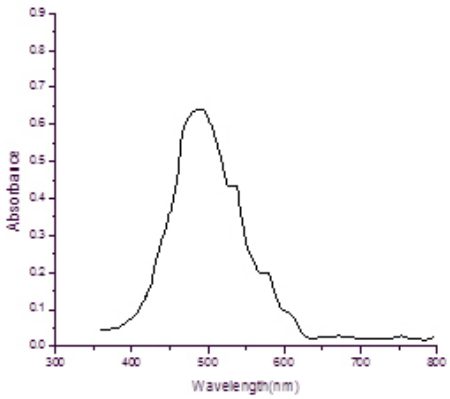


Fig.1: Absorbance spectra of the chelating ligand

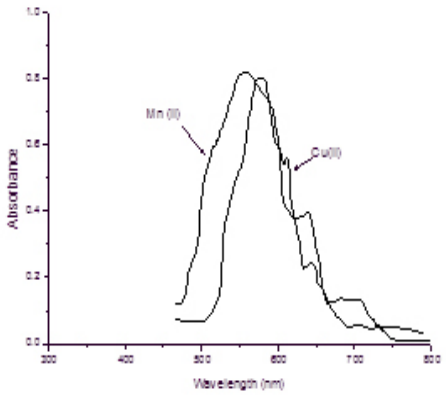


Fig. 2: Absorbance spectra for the Mn (II) -NDHBDED and Cu (II) - NDHBDED complexes

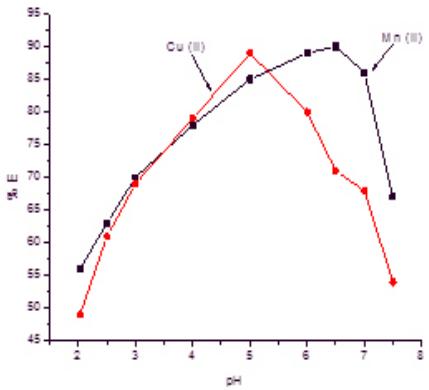


Fig. 3: Effect of pH for the extraction of both Mn (II) and Cu (II) ions

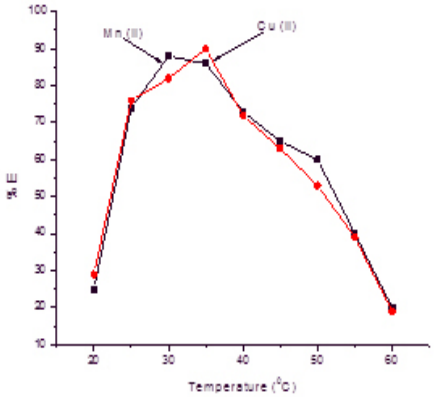


Fig. 4: Effect of temperature for the extraction of both Mn (II) and Cu (II) ions

(II) in the conc. range of 10-100 µg and 10-100 µg respectively. The formula of the complexes of Mn (II) and Cu (II) were ascertained by Job's method and molar ratios methods as 1:1. The analytical parameters of the solid phase spectrophotometric determination of Mn (II) and Cu (II) are given in [Table 1].

Effect of pH

In the quantitative recovery of the metal ions in the solid phase spectrophotometric (SPS) determination pH is a very key factor. The effect of pH for the percentage of extraction of Mn (II) and Cu (II) was investigated at a range 2 to 7.5. The quantitative extraction (> 90 %) found at the pH 6.5 and 5.5 respectively for Mn (II) and Cu (II). Hence, both of the above pH was chosen for the respective metal ions for further studies. Effects of pH on the percentage recovery of the metal ions were shown in Fig.3.

Effect of temperature

The influence of the temperature on the percentage of extraction of 10 µg/ml of each Mn (II) and Cu (II) was studied in the range of 20-60^0 C at pH range 5.0 - 6.5. The results showed in Fig.4, that the maximum percentage of sorption of Mn (II) is found at 30^0 C and Cu (II) is found at 35^0 C. Hence, for the extraction of both the metal ions, the temperature range was chosen for further studies.

Effect of amounts of NDHBDED

The effect of the reagent concentration impregnated with alumina on the quantitative extraction of metal ions was studied in the range of 0.1 to 1.0 mg. Results show that the extraction of the sorbent was increased on the addition of the reagent. The optimum amount of NDHBDED is at 0.5 mg, where more than 95 % of the metal ions extracted. The results are given in Fig.5.

Effects of metal ions concentration

The percentage extraction of the metal ions in the range of 10-100 µg/ml was studied at a fixed amount of the ligand (0.5 mg) on the solid matrix at pH 6.0. Almost 90 % of both the metal ions were extracted by the sorbent [Table 2].

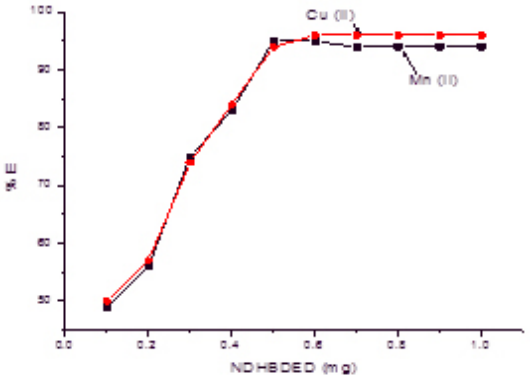


Fig. 5: Effect of the reagent concentration on the extraction of 10 µg/ml of Mn (II) & Cu (II) ions

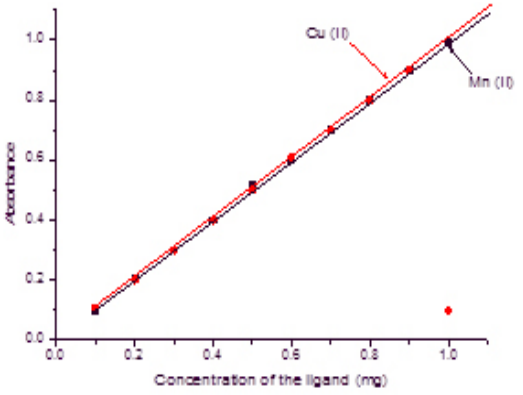


Fig. 6: Mole-Ratio of NDHBDED concentration to Mn (II) and Cu (II) ions

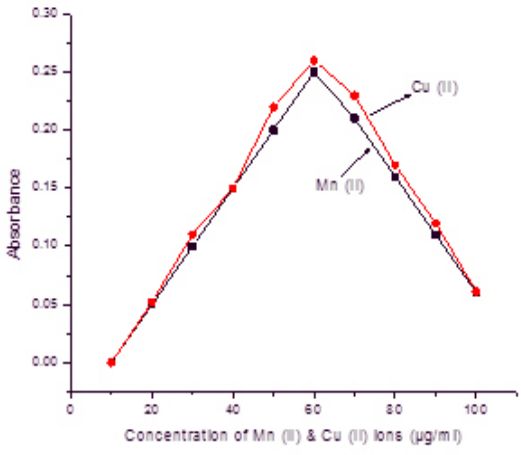


Fig. 7: Job's continuous variation method

The stoichiometry of the Mn (II) and Cu (II) - NDHBDED Complexes

The stoichiometry of the complexes with Mn (II) and Cu (II) ions were determined by Mole-Ratio method and by Job's method of continuous variation at fixed absorbance of λ_{max} 500 nm.

(a) Mole-Ratio method

The extraction of the metal ions were studied in the range 0.1 to 1.0 mg of the ligand concentration. The nature of the curves were straight line for both the metal ions which predicting the nature of the complexes are 1:1. The results shown in Fig. 6.

(b) Job's method of continuous variation

For fixed volume of the ligand concentration (0.5 mg) with the different concentration of the metal ions 10 – 100 µg/ml were studied. The natures of the curves predicting the nature of the complexs are 1:1. The results are shown in Fig.7.

Effects of Divers ions

The effects of various foreigns ions on the determination of Mn (II) and Cu (II) under optimum conditions was studied. The tolerance of the method of foreigns ions was investigated with solutions containing 1µg/ml each of Mn (II) and Cu

Table 1: Physical and Analytical Characteristics of Mn (II) & Cu (II) - NDHBDED Complexes

Parameters	Value	
	Mn (II)	Cu (II)
Molar absorbance (λ_{max})	590 nm	570 nm
Limit of Detection (µg/ ml)	0.1-1.0	0.1-10
Beer's law range	10-100 µg/ ml	10-100 µg/ ml
Molar absorptivity	$2.351x10^{-4}$ L mol^{-1} cm^{-1}	$2..225x10^{-4}$ L mol^{-1} cm^{-1}
Stability Constant (α)	$4.49x10^{7}$	$3.52X10^{7}$
pH	6.5	5.5
Temperature	30^0 C	35^0 C
Standard deviation	0.456	0.15
Composition (Metal:Ligand)	1:1	1:1
Sandell's Senstvity	0.004 µg/ cm^2	0.008 µg/ cm^2
Magnetic Moment (μ_{eff})	5.89 BM	1.723 BM

Table 2: Effect of Mn (II) and Cu (II) ions concentration on the percntage extraction of the solid sorbent matrix at pH 6.0 at room temperature

Mn (II)				Cu (II)			
Used (µg/ ml)	Extracted (µg/ ml)	% E	% RSD	Used (µg/ ml)	Extracted (µg/ ml)	% E	% RSD
10	7.5	75	0.12	10	7.4	74	0.21
20	15.2	76	0.14	20	15.04	75.2	0.11
30	22.8	76	0.15	30	22.89	76.3	0.09
40	31.8	79.5	0.09	40	31.2	78	0.23
50	41.75	83.5	0.11	50	42	84	0.35
60	51.12	85.5	0.14	60	51.6	86	0.17
70	61.88	88.4	0.08	70	60.9	87	0.27
80	70.88	88.6	0.06	80	70.48	88.1	0.16
90	79.65	88.5	0.12	90	79.2	88	0.2
100	88.5	88.5	0.12	100	88.2	88.2	0.21

(II) from several binary mixtures in a sample volume 50 ml and various amounts of foreigns ions. The determination of both the metal ions was possible in presence of Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Cr^{3+}, Sn^{2+}, Cl^-, Br^-, CO_3^{2-}, SO_4^{2-}, SO_3^{2-}, CH_3COO^-, NO_3^-, NO_2^-, CN^-. Few metal ions, such as Fe (III), Ni (II), Zn (II) and Pb (II) interfere only when present in the same concentration range. The results are presented in Table 3.

Effects of Eluents

Varoius volumes of different eluents were applied for determination of Mn (II) and Cu (II) under optimum conditions. For satisfactory results 3M HNO_3 has been used. Various volume of HNO_3 was used for extraction of each metal ions and it was found to increase by increasing its volumes. The results is shown in Table 4.

Analytical Application of the proposed method

Optimum pH subjected to the solid phase spectrophotometric (SPS) determination of each metal ions show the results as reported in Table 5. It clear that, the proposed method is suitable for Mn (II) and Cu (II) determination in real samples like tab water.

Table 3: Separation of 1µg/ml each of Mn (II) and Cu (II) from binary mixtures in a sample volume of 50 ml

Ions	Amount (mg)	% Recovery Mn (II)	% Recovery Cu (II)	Ions	Amount (mg)	% Recovery Mn (II)	% Recovery Cu (II)
Na^+	5	98.7	99.1	Cl^-	5	98.7	97
K^+	5	98.8	98.2	Br^-	5	97.2	98.5
NH_4^+	5	96.5	96	CO_3^{2-}	5	99.2	97.6
Ca^{2+}	5	97.6	97	SO_4^{2-}	5	96.8	98.7
Mg^{2+}	5	97.6	98.5	SO_3^{2-}	5	98.3	97.2
Al^{3+}	2.5	98.1	97.6	CH_3COO^-	2.5	95	99.2
Cr^{3+}	2.5	97.8	98.7	NO_3^-	2.5	96.3	96.8
Sn^{2+}	2.5	98	97.2	NO_2^-	2.5	98.7	98.3
Fe^{3+}	2.5	93	94.2	CN^-	2.5	95	95
Ni^{2+}	2.5	89.1	90.2	-	-	-	-
Zn^{2+}	2.5	90	90.6	-	-	-	-
Pb^{2+}	2.5	88.7	91	-	-	-	-

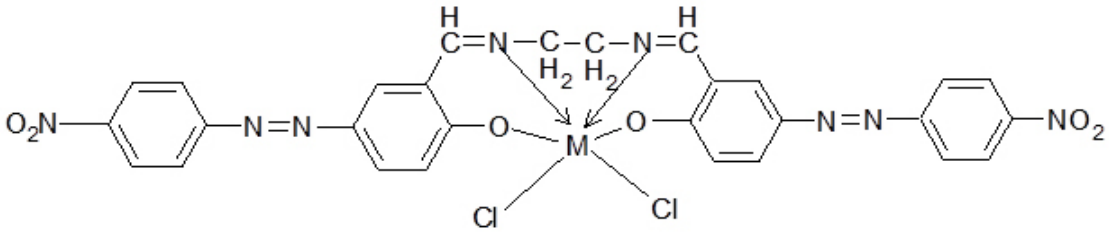
Table 4: Desorption of Mn (II) and Cu (II) by different eluents

Eluents	% Recovery Mn (II)	% Recovery Cu (II)
1 M HCl	75	64
2 M HCl	77	69
3 M HCl	80	73
1 M HNO_3	83	75
2 M HNO_3	86	79
3 M HNO_3	91	90
3 M CH_3COOH	41	45
3 M $H_2C_2O_4$	54	51

Table 5: Determination of Mn (II) and Cu (II) in real samples and tap water

Samples	Certified Value (µg/g)	Proposed method (µg/g)	% RSD
Soil	Mn (II) : 0.45	0.64	1.13
	Cu (II) : 0.11	0.34	3.09
Vegetable	Mn (II) : 0.05	0.045	0.9
	Cu (II) : 0.15	0.12	0.27
Tap water	Mn (II) : 0.002	0.0032	1.6
	Cu (II) : 0.015	0.002	0.13

The propposed structure of metal-ligand complexes



M = Mn (II) and Cu (II)

CONCLUSION

A simple and sensitive solid phase spectrophotometric method for the determination of Mn (II) and Cu (II) ions based on complexation. The method has been applied for the determination of these two metal ions in real samples and tap water. The wide applicability and simplicity of the proposed make it different from other existing methods.

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