

Sorption and Preconcentration of Zineb and Maneb using 1-(2-pyridylazo)-2-naphthol Anchored on Silica Nanoscavengers

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Abstract

A new analytical method in which 1-(2-pyridylazo)-2-naphthol anchored SiO₂ nanoparticles have been used as solid-phase extractant for the preconcentration of trace amounts of zineb and mane b in water and food samples. Conditions of the analysis such as preconcentration time, effect of pH, sample volumes, shaking time, elution conditions and effect of interfering ions for the recovery of analyte have been optimized. The extractant showed rapid kinetic sorption. The adsorption equilibrium of zineb and mane b on nanometer SiO₂-PAN was achieved in 15 min. Adsorption capacity and detection limit (3σ) of nanometer SiO₂-PAN has been found to be 42.52 and 50.80 μmol g⁻¹ and 0.93 and 0.60 μg L⁻¹ for zineb and mane b respectively under optimized conditions. Adsorbed zineb and mane b were easily eluted with 6 mL of 6 mol L⁻¹ hydrochloric acid. The method was applied for the determination of trace amounts of zineb and mane b in various food samples and spiked water samples.

Keywords:

Sorption; preconcentration; zineb; mane b; 1-(2-pyridylazo)-2-naphthol; silica; nanoscavenger

1. Introduction

Water, soil and food contamination has become a global environmental pollution problem. The major water, soil and food contaminants belong to the family of dithiocarbamates and organophosphate pesticides, which are ubiquitously used in agriculture. Pesticides are efficient tools for preventing crop losses due to plant pest and diseases. Dithiocarbamates are applied in agriculture as pesticide and in the rubber industry as vulcanization accelerators and anti-oxidants. Zineb (Zinc (II) ethylenebisdithiocarbamate) and Maneb (Manganese (II) ethylenebisdithiocarbamate) are the important dithiocarbamate fungicides [1-5]. Analytical methods are required for monitoring pesticides in various environmental samples. A number of methods such as spectrophotometry, high- performance liquid chromatography, extraction voltametry, titrimetry, polarography and gas chromatography have been reported for detection and analysis of zineb and mane b [6-13]. However, all of these methods suffer from the following disadvantages:

1. Methods other than gas chromatography are indirect and time consuming and their sensitivity is low.
2. Gas chromatographic methods are sensitive but suffer from a lack of selectivity because all dithiocarbamate pesticides evolve carbon disulphide on acid hydrolysis. Moreover, the dithiocarbamate decompositions are strongly dependent on temperature

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and on individual dithiocarbamate. The evolution of carbon disulphide requires >2h for the decomposition of dithiocarbamate.

3. High performance liquid chromatography (HPLC) methods involve the use of expensive and toxic solvents.

Solid phase extraction technique has been widely used in comparison with traditional extraction techniques; since it is simple, rapid and inexpensive, does not require the use of toxic organic solvents. Many substances such as organic chelate resin, silica gel, activated carbon, activated alumina, zeolites and microcrystalline materials are commonly used as adsorbents. The field of nanocomposite materials has received the attention, imagination and close scrutiny of scientists and engineer in recent years. These particles fall within the colloidal range, exhibiting typical colloidal properties. The size, surface structure and interparticle interaction of nanomaterials determine their unique properties and the improved performances and make their potential application in many areas. Nanoparticles such as TiO₂, Al₂O₃, ZrO₂, CeO₂ and modified silica nanoparticles have been used for the preconcentration of many metal ions and give promising results when used for trace element analysis of different samples [14-19]. But up till now, these nanoparticles have not been used for the preconcentration of dithiocarbamate. Here we present a relatively simple, rapid, sensitive and selective method in which chemically grafted SiO₂-PAN nanoparticles are used as nanoscavengers for zineb and maneb. These nanoscavengers (SiO₂-PAN) were prepared by sol-gel method and characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR). These nanoparticles have been used for the preconcentration of zineb and maneb prior to their determination by spectrophotometric method [20].

2. Experimental

2.1. Instruments and Apparatus

Absorbance of zineb and maneb were measured with UV-Vis Shimadzu-1700 spectrophotometer. The pH values were controlled by century Cp-901 digital pH meter. IR spectrum was recorded on a Perkin Elmer RXI FT-IR system. SEM micrograph was recorded on JEOL JSM 6100.

2.2. Reagents and Standards

Unless otherwise stated, all reagents used were of analytical grade. Sample solutions were prepared with double distilled deionized water. The 3-aminopropyltriethoxysilane (APTES) of GR grade was supplied by Acros Organics. 1-(2-pyridylazo)-2-naphthol (PAN) was obtained from Fluka. Nanometer SiO₂ was synthesized according to the method reported [21]. Zineb and maneb were prepared by adding a solution of zinc(II) and manganese(II) to a solution of disodium ethylenebisdithiocarbamate (Wilson laboratories) respectively. Stock solution of 0.1% zineb was prepared in 1.0 mol L⁻¹ sodium hydroxide working solution was prepared by appropriate dilution of stock solution. The pH adjustments were made with hydrochloric acid or ammonia and maintained with ammonia and ammonium chloride buffer. The glassware was washed with chromic acid and soaked in 5% nitric acid overnight and then cleaned with doubly distilled water before use.

2.3. Chemical Modification

Surface modification of SiO₂ nanoparticles were performed in a 250 mL flask. Nanometer SiO₂ (1 g) was dispersed into dry toluene (30 mL), and then 3-aminopropyltriethoxysilane (4 mL) was gradually added, with constant stirring. The mixture was refluxed for 6 hrs. The silylated nanometer SiO₂ was filtered off, washed with toluene and then with ethanol and finally dried at 60°C for 3 hrs. The product was transferred into the

flask, 100 mL absolute ethanol was added followed by 20 mL formaldehyde, 2.5 mL concentrated hydrochloric acid and 1 g of PAN and refluxed at 72°C for 4 hrs. Reaction mixture was filtered under vacuum, collected and stored.

2.4. General Procedure

Aliquots of sample solutions containing 0.65 and 0.54 μg of zineb and maneb were taken and pH 9.2 was adjusted with ammonia and ammonium chloride buffer. Then, 50 mg of PAN anchored silica nanoparticles were added, and the mixture was shaken vigorously for 15 min to facilitate adsorption. Zineb and maneb retained on the adsorbent were eluted with 6 mL of 6 mol L⁻¹ hydrochloric acid to get the Zn(II) and Mn(II) ions in solution respectively. Then, the solution was filtered and metal ions obtained were determined by standard spectrophotometric method [20].

3. Result and discussion

3.1. Characterization of SiO₂-PAN modified nanometer sized SiO₂.

The modification of nanometer-sized material is usually required in order to prevent a conglomeration of particles and to improve its consistency in relation to other materials, such as organic polymers. The modification of nanometer-sized materials can improve the selectivity towards metal ions. The modified nanometer SiO₂-PAN was characterized by SEM and FT-IR.

3.2. Scanning Electron Microscopy

The average diameter of the nanoparticles SiO₂, SiO₂-APTES and SiO₂-PAN was 100 nm, 1 μm and 2 μm confirmed by Scanning Electron Microscopy. From the SEM micrographs, it is clear that the surface of the nanoparticles is smooth so that there is proper chemical modification occurred for the preconcentration of zineb and maneb. Fig.1 (A, B, C) reveals the average size of SiO₂ nanoparticle, SiO₂-APTES and SiO₂-PAN respectively.

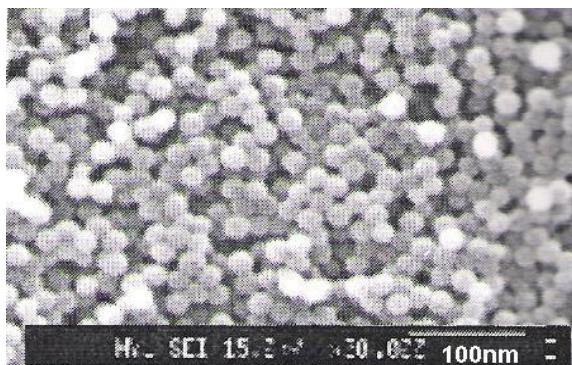


Fig 1. a. SEM micrograph of SiO₂ nanoparticle.

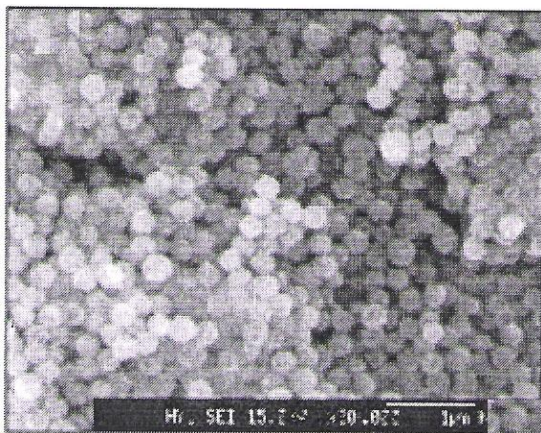


Fig 1. b. SEM micrograph of SiO₂-APTES nanoparticle.

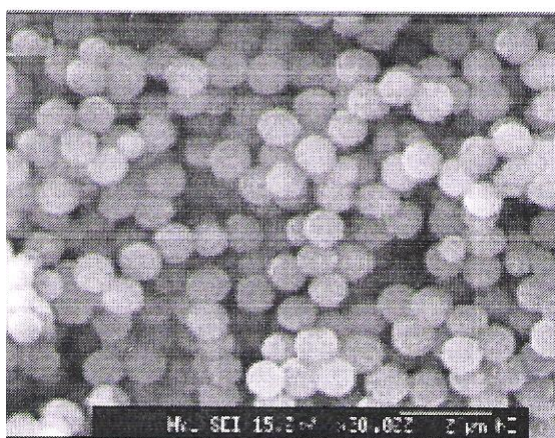


Fig 1. c. SEM micrograph of SiO₂-PAN nanoparticle.

3.3. FT-IR Spectrum Analysis

FT-IR spectra of 1-(2-pyridylazo)-2-naphthol, nano-SiO₂, nanometer SiO₂-PAN, nano-SiO₂-APTES respectively. Fig. 4 shows the FT-IR spectra of PAN, nano-SiO₂-PAN, nano-SiO₂-APTES and nano-SiO₂. Fig. 2(a,b,c) reveals that main absorption peaks of nanometer SiO₂ (3448.0, 1642.5, 1404, 1070.2, 964.2, 798.8 cm⁻¹) are in agreement with standard spectrum of SiO₂ [27]. Many new peaks appeared in FT-IR spectrum of SiO₂-PAN which are assigned as follows: the peak at 1683.5 cm⁻¹ is due to N=N stretching vibration and 1590, 1540, 1500 and 695.9 cm⁻¹ peaks are due to C=C stretching vibration of the benzenoid and pyridyl unit in 1-(2-pyridylazo)-2-naphthol at, peak at 1381.6 cm⁻¹ due to CH₂ shear deformation vibration, the peak at 1329.4 cm⁻¹ is C-N stretching vibration for the benzenoid unit in 1-(2-pyridylazo)-2-naphthol, the peak at 1098.1 cm⁻¹ is caused by C-O stretching vibration in 1-(2-pyridylazo)-2-naphthol. The above experimental results suggest that nanometer SiO₂ has been successfully modified by 1-(2-pyridylazo)-2-naphthol.

3.4. Effect of pH on Enrichment Recovery

The adsorption of zineb and maneb on nanometer SiO₂-PAN has been studied in pH range 1.2 to 10.0 by general procedure. The results of effect of pH on the recoveries of the metal ions are shown in Fig. 3. Quantitative recovery (≥95%) has been found for zineb and maneb in the pH range of 7.0-10.0.

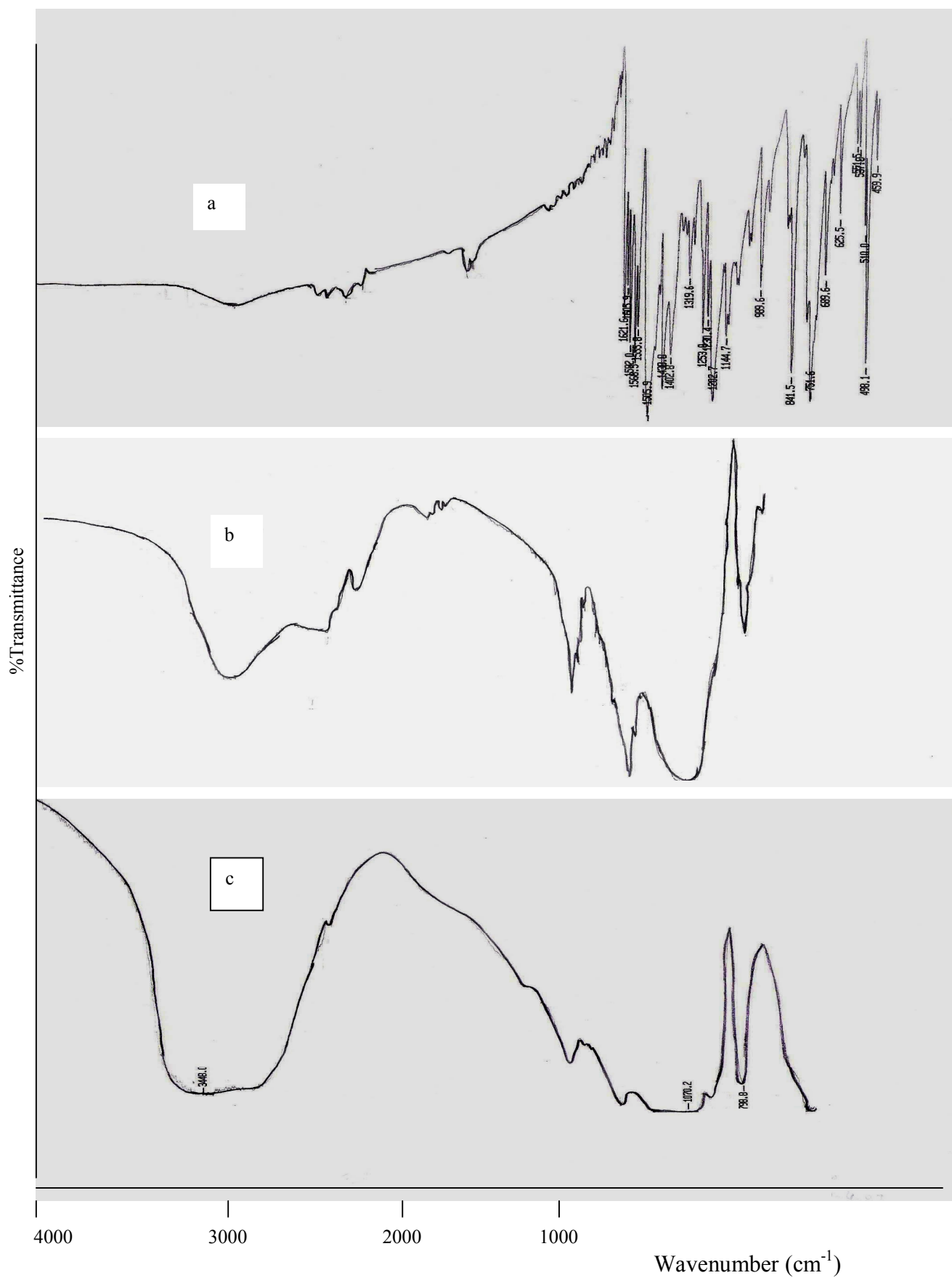


Fig 2. FTIR spectra (a) PAN (b) nanometer SiO_2 -PAN (c) nanometer SiO_2 .

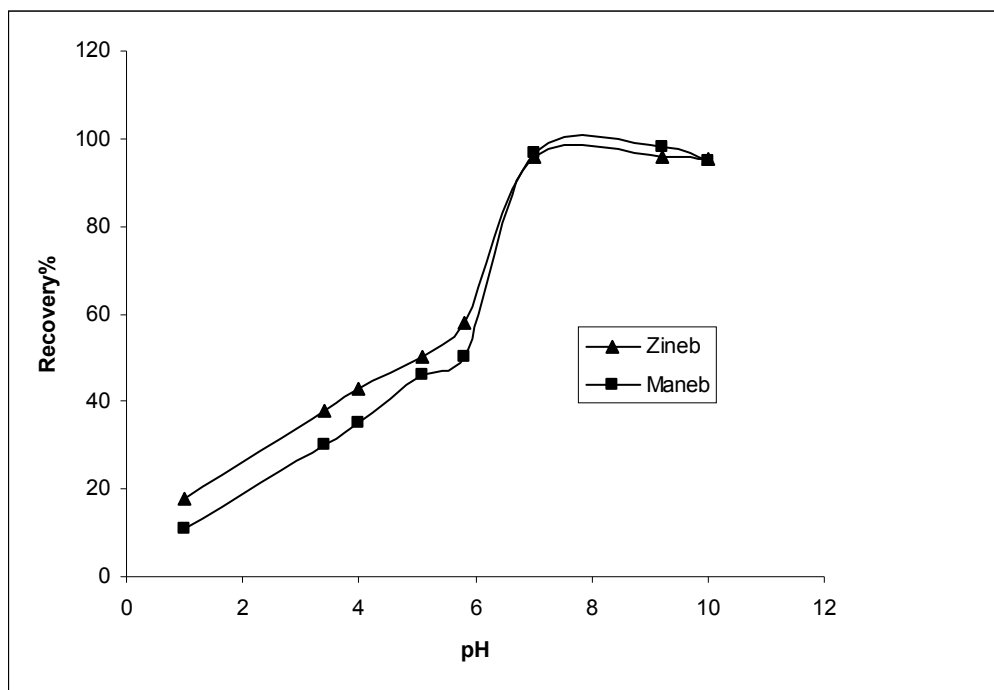


Fig. 3. Effect of pH on recoveries of analytes

3.4. Effect of nanometer SiO₂-PAN Amount

To test the effect of amount of extractant on quantitative retention of analyte, different amounts (10-120 mg) of SiO₂-PAN nanoparticles were added into the solution following the general procedure. Quantitative removal of the zineb and maneb was obtained in the range of 25-100 mg of SiO₂-PAN nanoscavengers. With amounts of extractant less than 25 mg or greater than 100 mg quantitative removal was not obtained. Extractant amount larger than 100 mg may prevent the elution of the retained zineb and maneb. 50 mg of nanomaterial SiO₂-PAN as extractant was used for further studies.

3.5. Effect of Shaking Time

The adsorption of zineb and maneb on 50 mg of nanometer SiO₂-PAN was studied for different shaking time (5-30 min). The results indicated that the extraction percentage greater than 95% of zineb and maneb was achieved in 15 min.

3.6. Effect of Eluent Concentration and Volume

Since the adsorption of zineb and maneb on nanometer SiO₂-PAN at pH ≤ 1 is found to be negligible, elution will be favored in acidic solution. So, various concentrations of hydrochloric acid were studied for desorption of retained zineb and maneb and quantitative recoveries (>95%) of Zn (II) from zineb and Mn(II) from maneb were obtained using 6 mL of 6 mol L⁻¹ hydrochloric acid as eluent. Therefore, in subsequent experiments 6 mL of 6 mol L⁻¹ of hydrochloric acid was used as eluent. The results of effect of eluent concentration and volume are given in Table 1.

3.7. Adsorption Capacity (Q_s)

The adsorption capacity is an important factor as it determines how much adsorbent is quantitatively required to concentrate the analytes from a given solution. A breakthrough curve was obtained by plotting the concentration (mgL⁻¹) vs. the μmol of zineb and maneb adsorbed per gram is given in Fig. 4. From the breakthrough curve the amount of modified

nanometer SiO₂-PAN for zineb and maneb was found to be 42.52 and 50.80 $\mu\text{mol g}^{-1}$ respectively under optimized conditions.

Table 1. Effect of Concentration of Hydrochloric Acid Solution on Elution of Zineb and Maneb.

Concentration of Eluent, mol L^{-1}	Recovery, %	
	Zineb	Maneb
1.0	30.0	25.3
2.0	58.5	47.0
4.0	65.7	68.8
6.0	97.8	96.3
8.0	90.2	91.3
10.0	80.0	75.2

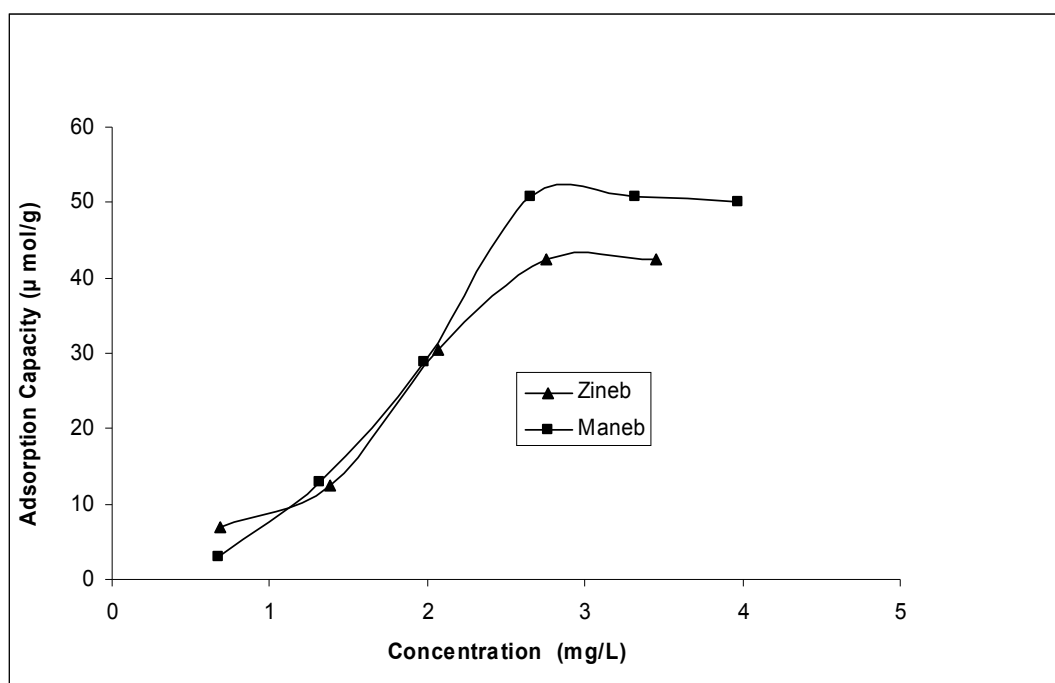


Fig. 4. Adsorption capacities of analytes on nanometer SiO₂-PAN.

3.8. Effect of Sample Volume

In order to explore the possibility of concentrating low concentration of analytes from large volumes, the effect of sample volume on the retention of pesticides was also investigated. For this purpose, 20, 50, 100, 150, 200, 250, 300 and 350 mL of the sample solutions containing 1 μg both for zineb and maneb were shaken, quantitative recoveries ($\geq 95\%$) were obtained for sample volume of $\leq 300\text{mL}$ for zineb and maneb. Therefore, a preconcentration factor was 50 for zineb and maneb has been obtained. The results of effect of sample volume on recoveries are shown in Fig. 5.

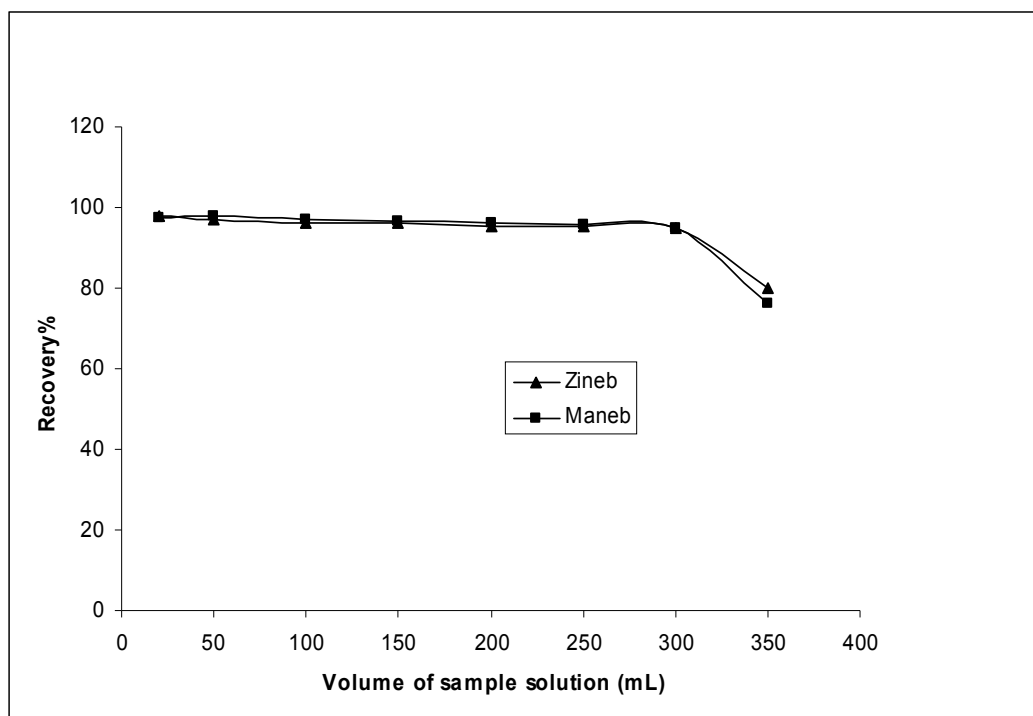


Fig 5. Effect of volume of sample solution on recovery %.

3.9. Effect of Coexisting Ions

The effect of various diverse ions on the adsorption of a solution containing 0.65 and 0.54 $\mu\text{g mL}^{-1}$ of zineb and maneb was studied. An ion was considered to interfere when its presence produced a variation in the adsorption of the sample greater than 5%. However, ethylenediamine tetraacetate ion (EDTA) interfered strongly in determination of both zineb and maneb. The tolerance amounts of cations and anions are given in Table 2.

Other dithiocarbamate pesticides such as dibam (sodium dimethyldithiocarbamate), vapam (sodium monomethyldithiocarbamate), nabam (sodium ethylenebisdithiocarbamate), and sodium N-methylanilinecarbodithioate, potassium morpholine-4-carbodithioate did not interfere in the determination of maneb and zineb.

Table 2. Effect of Volume of Hydrochloric Acid on Elution of Zineb and Maneb.

Volume of eluent, mL	Recovery, %	
	Zineb	Maneb
2.0	83.2	70.5
4.0	87.5	80.3
5.0	92.4	87.6
6.0	97.8	96.3
8.0	89.4	84.4
10.0	82.3	75.8

4. Analytical Precision and Detection Limit

Under these optimized conditions, zineb and maneb standard solutions were enriched and analyzed by general procedure. The relative standard deviation (RSD) of the method was

3.1 and 2.0 % for the determination of 0.65 μg and 0.54 μg for zineb and maneb respectively. The detection limit of this method for zineb and maneb was 0.93 and 0.60 $\mu\text{g L}^{-1}$.

5. Applications

The method was applied for the determination of zineb and maneb in crops, vegetables (grain, potato and cabbage) and spiked water samples. Since in the present method zineb and maneb were determined in the form of Zn(II) and Mn(II) so these metal ions already present in the crops were detected originally and amount (μg) of Zn(II) was found to be 10.40, 6.5 in grains and potatoes and amount of Mn(II) was found to be 7.3, 20.50 in potatoes, cabbage respectively. A known amount of zineb and maneb were crushed with 10gm of vegetable or crops with a pestle and mortar and shaken mechanically with 100 mL of DMSO for 1hrs. The mixture was filtered; the residue in the funnel was washed with DMSO. The filtrate was collected and the zineb and maneb content were determined by general procedure. The results of the determination of zineb and maneb in crops, vegetables and spiked water samples are given in Table 3.

Table 3. Effect of Diverse Anions on the Determination of Zineb and Maneb

Anion	Tolerance limit, mg	
	Zineb	Maneb
Chloride	470	450
Bromide	100	90
Fluoride	490	500
Sulfate	350	360
Phosphate	20	15
Oxalate	10	10
Nitrate	100	100
Citrate	20	20
Metabisulfite	30	30

6. Conclusion

1-(2-pyridylazo)-2-naphthol- anchored silica nanoparticles were prepared and used as solid sorbent for preconcentration of zineb and maneb for the first time prior to their determination. These analytes can be easily screened at $\mu\text{g L}^{-1}$ level with preconcentration times of 15 min and preconcentration factor of 50 for both zineb and maneb.

The 1-(2-pyridylazo)-2-naphthol- anchored silica nanoparticles have been found to be much selective for preconcentration of these analytes and showed great capacity, and rapidness. The proposed method has been used for the determination of these metal ions in various food and water samples. The results of determination have been found to be accurate and reproducible.

Table 4. Effect of Diverse Cations on the Determination of Zineb and Maneb.

Cation	Tolerance limit, mg	
	Zineb	Maneb
Cr(III)	100	100
Mg(II)	750	800
V(V)	30	30
Ni(II)	^a	^a
Cu(II)	500 ^a	470 ^a
Co(II)	760 ^b	800 ^b
Zn(II)	--	^c
Mn(II)	^d	---
Mo(II)	150	150
Fe(III)	100	^a

^a masked with 2mL of 1% sodium tartrate, ^b masked with 1.0mL of 1% hydroxylamine hydrochloride, ^c masked of with 1.0mL of 5% of sodium fluoride ^dmasked with potassium bromide.

Table 5. Determination of Zineb in Grains and Potatoes.

Crop	Added, μg	Found, μg	Recovery, %
Grain	0.0	10.40	----
	10.0	20.26	98.65
	20.0	19.94	95.67
Potato	0.0	6.65	---
	10.0	16.42	98.76
	20.0	26.40	98.46

Table 6. Determination of Maneb in Vegetables.

Crop	Added, μg	Found, μg	Recovery, %
Potato	0.0	7.3	---
	10.0	17.10	97.26
	20.0	27.22	98.90
Cabbage	0.0	20.50	---
	10.0	30.22	98.63
	20.0	40.30	99.02

Table 7. Determination of Zineb and Maneb in Spiked Water Samples.

Sample	Added, μg	Found, μg	Recovery, %
Zineb	10.0	9.75	97.5
	20.0	19.80	99.0
Maneb	10.0	9.80	98.0
	20.0	19.30	99.3

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