Research Article

Separation and Preconcentration of Trace Amounts of Manganese and Nickel from Natural Water Samples by a Diimine Derivative Schiff Base-Coated Silica-Gel Minicolumn

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An efficient method for preconcentration of trace amounts of Mn (II) and Ni (II) ions by using a minicolumn (10 mm × 30 mm i.d.) filled with a diimine derivative Schiff base on silica-gel has been reported. The retained analytes on the column were recovered with 5 mL of mixture of nitric acid 5 mol L^{-1} and methanol (1 : 1) and were determined by a flame atomic absorption spectrometer. Different factors including pH of sample solution, sample volume, amount of sorbent, eluent volume, and interference of other ions have been studied and the optimized conditions developed were utilized for the trace determination of Mn (II) and Ni (II) in natural water samples. The recoveries for the analytes under the optimum working conditions were higher than 98%. The relative standard deviations of the determinations (10 replicate analyses) at 25 $\mu g\, L^{-1}$ of Mn (II) and Ni (II) were 2.5% and 2.3%, respectively. The limit of the detection (3s, n = 10) for analytes were found to be 0.20 $\mu g\, L^{-1}$ for Mn (II) and 0.15 $\mu g\, L^{-1}$ for Ni (II). The proposed method was applied to the analysis of natural water samples with satisfactory results.

1. Introduction

The importance of the determination of trace metal concentration in natural water samples is increasing in contamination monitoring studies. Flame atomic absorption spectrometry (FAAS) is a simple and well available technique for the determination of heavy metals in the natural water samples. However its main problem is the low sensitivity for trace metals at $\mu g\, L^{-1}$ level. This limitation can be overcome by the use of a preconcentration procedure [1]. Among different preconcentration and/or separation techniques, solid phase extraction (SPE) using batch, and column techniques in which compounds, elements, or species of elements interested with are retained by sorption on different solid-phases and eluted with acids or other reagents which have been widely used [2, 3]. The application of solid phase extraction technique for preconcentration of trace metals from different samples results in several advantages such as the minimal waste generation, reduction of sample matrix effects and sorption of the target species on the solid surface in a more stable chemical form [4]. The normal and selective solid phase extractors are those derived from the immobilization of the organic compounds on the surface of solid supports. Naphthalene [5], XAD-2 [6], polyurethane foams [7], XAD-4 resin [2], silica-gel, alumina, magnesia, and zirconia are the major solid matrixes that have been used to immobilize the target organic modifiers on their surfaces [8]. Silica-gel is the most widely used solid support due to the well-documented thermal, chemical, and mechanical stability properties compared to other organic and inorganic solid supports [9]. The surface of silica-gel is characterized by the presence of silanol groups, which are known as weak ion exchangers, causing low interaction, binding, and extraction of the target analytes [10]. For this reason, modification of the silica-gel surface with certain functional groups has successfully been employed to produce the solid phase with certain selectivity characters [11].

Two approaches are known for loading the surface of solid phases with certain organic compounds and these are defined as the chemical immobilization which is based on chemical

bond formation between the silica-gel surface groups and those of the organic modifier, and the other approach is known as the physical adsorption in which direct adsorption of the organic modifier with the active silanol groups takes place [8].

In this paper we report the synthesis of a diimine derivative Schiff base and its use as modifier for solid phase extraction of Ni (II) and Mn (II) from water samples. To the best of our knowledge, silica-gel minicolumn modified by diimine derivative Schiff base has not been employed previously for selective separation and preconcentration of Ni (II) and Mn (II) from natural water samples.

2. Experimental

2.1. Reagents. Analytical reagent-grade chemicals and doubly distilled water were used. All glassware was soaked in 10% nitric acid for at least 24 h and washed with water and dried in a dust-free environment. Silica-gel (60–200 μm) was received from Riedel de Haën, Hannover, Germany. Stock solution of 1000 μg mL^{-1} of Ni (II) and Mn (II) was prepared by dissolving appropriate amounts of Ni(NO$_3$)$_2$, 6H$_2$O and Mn(NO$_3$)$_2$, 4H$_2$O (Merck, Darmstadt, Germany) in concentrated nitric acid and diluting to 100 mL with water separately. Working solutions were prepared from the stock solution by serial dilutions with distilled water.

2.2. Synthesis of Bis-(2-Hydroxyacetophenone)-2,2-Dimethyl-1,3-Propane Diimine (Diimine Derivative Schiff Base). 2-hydroxyacetophenone (0.02 mol, 2.72 g) was mixed with 150 mL of distilled ethanol in a 500 mL round bottom flask, which was stirred using a magnetic stirrer. 2,2-Dimethyl-1,3- propanediamine (0.01 mol, 1.02 g) dissolved in 25 mL of distilled ethanol was added drop by drop using a dropping funnel to the above solution. The contents were refluxed for 2 h to get a yellow solid precipitate of Schiff base ligand, which was cooled, filtered, washed with petroleum ether, and dried. The ligand was then recrystallised from ethanol [12].

The calculated contents of elements in C$_{21}$H$_{26}$N$_2$O$_2$ were as follows:

C, 74.52; H, 7.74; N, 8.28%.

The obtained contents were as follows:

C, 73.94; H, 7.68; N, 8.41%.

IR (KBr): ν (C=N) 1630, ν (C-O) 1283.

2.3. Apparatus. A metrohm 713 pH meter was used for measuring the pH of the solutions. Metal determinations were performed using a Perkin-Elmer Model 3110 flame atomic absorption spectrometer. All measurements were carried out in air/acetylene flame. The operating parameters for elements were set as recommended by the manufacturer. A Jenway 1002 stirrer was used for stirring the solutions.

2.4. Preparation of Silica-Gel Loaded a Diimine Derivative Schiff Base. A 5 g portion of silica-gel was added to 11 mL of 10^{-2} mol L^{-1} diimine derivative Schiff base in acetone.

The mixture was vigorously stirred at room temperature to complete the solvent evaporation (approximately 30 min). The solid mass was homogenized in a mortar and stored in amber glass flasks.

2.5. Column Preparation. A minicolumn (10 mm × 30 mm i.d.) with a glass wool over its stopcock was used as a minicolumn for the study. A total of 0.5 g diimine derivative Schiff base-coated silica-gel was placed into the column. A small amount of glass wool was placed on top to avoid disturbance of the adsorbent during the sample passage. The column was preconditioned by the blank solution having same pH with the sample solution prior to use.

2.6. Recommended Procedure. A given volume of aqueous sample up to 1000 mL containing Mn (II) and Ni (II) ions, after adjustment to pH = 4, was loaded into the diimine derivative Schiff base-coated silica-gel minicolumn at a flow rate of 5 mL min^{-1}. Then, the adsorbed metal was eluted with 5 mL of mixture of 5 mol L^{-1} nitric acid and methanol (1 : 1) at an elution rate of 2 mL min^{-1}. The Ni (II) and Mn (II) ions concentration in eluate were determined by FAAS.

3. Results and Discussion

In order to obtain a high recovery, the effect of different parameters, influencing the complex formation and the extraction conditions, were optimized. These parameters were pH of sample solution, sample volume, and flow rate, amount of sorbent, eluent type, volume and flow rate, and interference of various ions. A volume of 200 mL of water samples was used for the optimization of parameters. Finally, these optimal conditions were applied to extract and detect Mn (II) and Ni (II) in the natural water samples.

3.1. Effect of pH. The effect of the pH of the sample solutions on adsorption of Mn and Ni was evaluated by adjusting the pH in a range of 1–12 with HCl or NaOH solution. Figure 1 shows the effect of pH on the recovery of the studied metal ions. As can be seen, the extraction recovery of Ni and Mn complexes increases up to pH = 3, and then remains constant in the pH range 3–5. The Competition between protons and nickel ions could explain the weak recovery in acid medium. Therefore, the working pH was chosen as 4 for the following experiments.

3.2. Effect of Sample Flow Rate. Since the retention of elements on the sorbent depends on the flow rate of the metal solutions, the influence of flow rate for sample solutions on the retention of the trace metals was investigated over the range 1–15 mL min^{-1} under the optimum conditions. As can be seen in Figure 2, the recovery begins to decrease with an increase in the flow rate when that is greater than 7 mL min^{-1}. Therefore, flow rate of the sample was chosen as 5 mL min^{-1} for the following measurements.
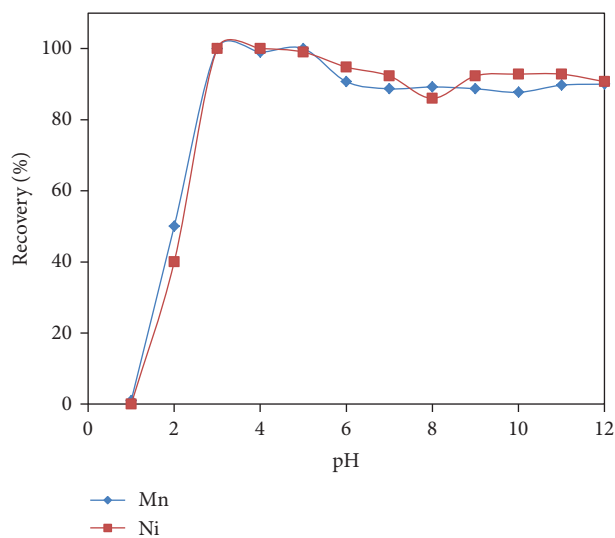
Figure 1: Effect of pH on the adsorption of Ni (II) and Mn (II) on Schiff base-coated silica-gel. Concentration of standard solution Mn (II) and Ni (II), $25\,\mu$g L^{-1}. Sample flow rate, 5 mL min^{-1}. Eluent type, 5 mL mixture of nitric acid 5 mol L^{-1}, and methanol (1 : 1). Elution flow rate, 2 mL min^{-1}.
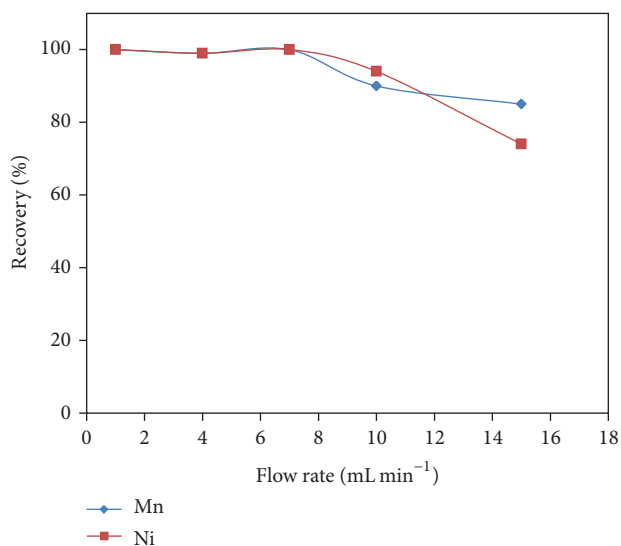

Figure 2: Effect of flow rate on the adsorption of Ni (II) and Mn (II) on column. Concentration of standard solution Ni (II) and Mn (II), $25\,\mu$g L^{-1}, pH = 4. Eluent type, 5 mL mixture of nitric acid 5 mol L^{-1}, and methanol (1 : 1). Elution flow rate, 2 mL min^{-1}.

3.3. Effect of Elution Conditions.

The eluent type, volume, and the flow rate could affect the efficiency of the elution heavily. To obtain quantitative recovery, the effect of eluent type and volume on preconcentration was investigated using various eluting solutions. The results are shown in Table 1. The results show that 5 mL mixture of nitric acid 5 mol L^{-1} and methanol (1 : 1) was sufficient for complete elution. The effect of eluent flow rate on recovery was investigated in the range of 0.5–5 mL min^{-1}. The results showed that quantitative
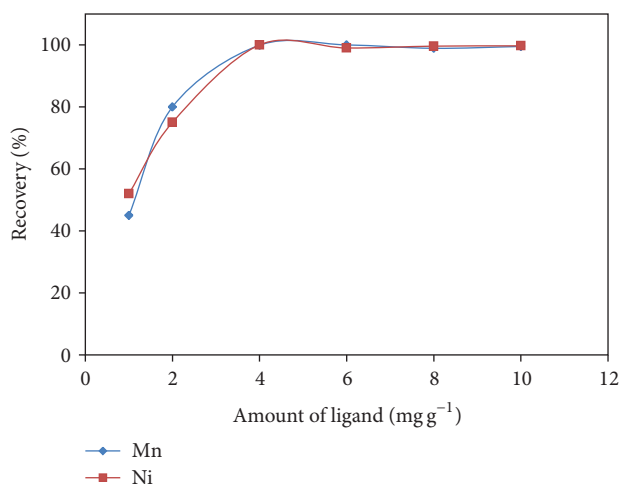

Figure 3: Effect of amount of diimine derivative Schiff base (ligand) on the recovery of Ni (II) and Mn (II) on column. Concentration of standard solution Ni (II) and Mn (II), $25\,\mu$g L^{-1}, pH = 4, sample flow rate, 5 mL min^{-1}. Eluent type, 5 mL mixture of nitric acid 5 mol L^{-1}, and methanol (1 : 1). Elution flow rate, 2 mL min^{-1}.

recoveries could be obtained with elution flow rate up to 2 mL min^{-1}. Thus, the elution flow rate of 2 mL min^{-1} was used in the following experiments.

3.4. Effect of Amount of Ligand and Silica-Gel.

In order to determine the concentration of diimine derivative Schiff base required for quantitative recoveries of investigated metal ions, the amount of diimine derivative Schiff base (ligand) was investigated in the range of 1–10 mg g^{-1} (milligram of diimine derivative Schiff base per gram of silica-gel). Firstly, some works were carried out without ligands at optimum pH 4 and it was observed that the Mn (II) and Ni (II) ions were not quantitatively recovered in the absence of ligands. Therefore, the studies were performed with the various amounts of diimine derivative Schiff base and results are presented in Figure 3. It can be seen that the recoveries of the metal ions increased with increasing concentration of diimine derivative Schiff base added and reached a constant value with at least 4 mg g^{-1}. On this basis, 5 mg g^{-1} of diimine derivative Schiff base was chosen to account for other extractable species that might potentially interfere with the assaying of metal ions.

3.5. Capacity of the Sorbent.

In order to study the adsorptive capacities of modified sorbent for Ni (II) and Mn (II) batch method were used. 100 mL of solution containing 20 mg of Ni (II) and Mn (II) was added to 0.5 g diimine derivative Schiff base-coated silica-gel, at pH = 4. After shaking for 1 h, the mixture was filtered. The supernatant solution was diluted and determined by flame atomic absorption spectrometry. The capacity of sorbent was found 0.82 mg g^{-1} for Mn (II) and 0.87 mg g^{-1} for Ni (II).

3.6. Effect of Volume of Sample Solution.

The effects of changes in the volume of sample solution passed through the

TABLE 1: Effect of eluent type and volume on recovery of Ni (II) and Mn (II) Sample flow rate, 5 mL min^{-1}. pH = 4. Eluent type, 5 mL mixture of nitric acid 5 mol L^{-1}, and methanol (1 : 1). Elution flow rate, 2 mL min^{-1}.

Eluent	Volume (mL)	Recovery (%)	
		Mn	Ni
1 mol L^{-1} HCl	2	45.2	48.3
	5	46.8	49.2
	10	47.3	53.2
2 mol L^{-1} HCl	2	45.6	55.0
	5	48.9	56.0
	10	50.2	56.9
1 mol L^{-1} HNO$_3$	2	50.0	53.1
	5	58.7	56.8
	10	59.6	57.9
2 mol L^{-1} HNO$_3$	2	60.0	58.0
	5	63.4	59.4
	10	68.2	63.7
1 mol L^{-1} HNO$_3$ + Methnol (1 : 1)	2	70.0	69.8
	5	72.0	73.0
	10	75.6	75.8
2 mol L^{-1} HNO$_3$ + Methanol (1 : 1)	2	75.4	74.9
	5	78.6	76.9
	10	81.0	80.0
5 mol L^{-1} HNO$_3$ + Methanol (1 : 1)	2	89.5	85.3
	5	99.9	99.5
	10	99.8	99.9

TABLE 2: Effect of volume of sample solution on the recovery of Mn (II) and Ni (II) Sample flow rate, 5 mL min^{-1}. pH = 4. Eluent type, 5 mL mixture of nitric acid 5 mol L^{-1}, and methanol (1 : 1). Elution flow rate, 2 mL min^{-1}.

Added (μg)	Mn, Ni	20	20	20	20	20
Sample passed (mL)	Mn, Ni	25	100	250	500	1000
Recovered (μg)	Mn	19.9	19.8	19.8	19.6	19.7
	Ni	19.8	19.9	19.7	19.7	19.8
Recovery (%)	Mn	99.5	99.0	99.0	98.0	98.5
	Ni	99.0	99.5	98.5	98.5	99.0
Preconcentration factor	Mn, Ni	5	20	50	100	200

TABLE 3: Tolerance limits for coexisting ions on the recovery of 25 μg L^{-1} Mn (II) and Ni (II).

Coexisting ions	Ion/target ions ratio (w/w)
Na$^+$, K$^+$, Li$^+$	2000
Sr^{2+}, Sc^{3+}, Rh^{3+}	87
Ca^{2+}, Ba^{2+}, Be^{2+}, Pd^{2+}	80
ClO$_4^-$, Zn^{2+}, Fe^{3+}, Cd^{2+}	50
Pb^{2+}	30
Co^{2+}, Ag$^+$, Mg^{2+}	20
Al^{3+}	15
Cr^{3+}	10
Hg^{2+}	8
Cu^{2+}	3

minicolumn, packed with a diimine derivative Schiff base-coated silica-gel on the recovery of Mn (II) and Ni (II) was examined (Table 2). No decline in the recovery of Mn (II) and Ni (II) was observed up to a volume of 1000 mL, the maximum tested in these experiments. In the present work, as the elution volume is 5 mL the preconcentration factor is obtained up to 200.

3.7. Interferences Effects. Preconcentration procedures for trace metals can be strongly affected by the matrix constituents of the samples. For this reason, the reliability of the proposed method was examined in the presence of possible matrix ions of the natural water samples. The tolerance of coexisting ions, defined as the largest amount yielding a change of less than 5% in the adsorption efficiency of 25 μg L^{-1} of Mn (II) and Ni (II), are given in Table 3.

TABLE 4: Determination of Ni (II) and Mn (II) in natural water samples (N = 3, Sample volume: 1000 mL, eluent volume: 5 mL).

Sample	Added (μg L^{-1})		Found (μg L^{-1})		Relative Recover (%)	
	Mn	Ni	Mn	Ni	Mn	Ni
River water[a]	0.0	0.0	14.10 ± 0.30[f]	8.70 ± 0.20	—	—
	10.0	10.0	24.30 ± 0.60	19.10 ± 0.50	102.0	104.0
	20.0	20.0	33.80 ± 0.80	28.90 ± 0.70	98.5	101.0
River water[b]	0.0	0.0	13.20 ± 0.30	6.50 ± 0.18	—	—
	10.0	10.0	23.00 ± 0.50	16.30 ± 0.40	98.0	98.0
	20.0	20.0	33.50 ± 0.90	26.20 ± 0.60	101.5	98.5
Tap water[c]	0.0	0.0	5.80 ± 0.16	2.30 ± 0.06	—	—
	10.0	10.0	15.60 ± 0.40	12.40 ± 0.30	98.0	101.0
	20.0	20.0	25.70 ± 0.60	22.50 ± 0.60	99.5	101.0
Mineral water[d]	0.0	0.0	3.20 ± 0.08	1.10 ± 0.03	—	—
	10.0	10.0	12.90 ± 0.30	10.70 ± 0.30	97.0	96.0
	20.0	20.0	22.50 ± 0.50	20.60 ± 0.40	96.5	97.5
Sea water[e]	0.0	0.0	9.60 ± 0.20	4.80 ± 0.14	—	—
	10.0	10.0	19.10 ± 0.40	14.50 ± 0.30	95.0	97.0
	20.0	20.0	28.70 ± 0.70	24.10 ± 0.60	95.5	96.5

[a] Sefidrood river, Iran.
[b] Karaj river, Iran.
[c] Drinking water system of Tehran, Iran.
[d] Damavand mineral water, Iran.
[e] Caspian sea water, Anzali, Iran.
[f] mean ± standard deviation.

TABLE 5: Comparison of the proposed SPE method with other SPE methods reported in the literature.

Adsorbent	Element	LOD[a] (μg L^{-1})	R.S.D.[b] (%)	PF[c]	Sample volume (mL)	Reference
Coated alumina	Mn, Ni	0.27, 0.28	—	75	150	[13]
Nanometer TiO$_2$	Mn, Ni	0.52, 1.78	2.4, 5.5	50	50	[14]
Chelating resin	Mn, Ni	0.20, 0.71	—	150	1500	[15]
Chromosorb 108	Mn, Ni	0.33, 0.44	1.8, 1.4	80	400	[16]
Coated silica-gel	Mn, Ni	0.20, 0.15	2.5, 2.3	200	1000	Present work

[a] Limit of detection, [b] Relative standard deviation, [c] Preconcentration factor.

3.8. *Figures of Merit.* For determining figures of merit a volume of 1000 mL of water samples was used for the analysis. Under the optimum experimental conditions, the calibration graph for the determination of Mn (II) and Ni (II) were linear from 0.7 to 50 μg L^{-1} and from 0.5 to 35 μg L^{-1}, respectively. The repeatability of measurements was tested for a concentration of 25 μg L^{-1} of Mn (II) and Ni (II). The relative standard deviations (10 replicate analyses) were 2.5% for Mn (II) and 2.3% for Ni (II). Detection limits defined as three times of the standard deviation of blank were 0.20 μg L^{-1} for Mn (II) and 0.15 μg L^{-1} for Ni (II).

3.9. *Analysis of Mn (II) and Ni (II) in Natural Waters.* The present method was applied to the extraction and determination of Mn (II) and Ni (II) in various natural water samples. A volume of 1000 mL of water samples was used for the analysis. The results are summarized in Table 4. The suitability of the proposed method for the analysis of natural water samples was checked by spiking samples with different levels of Mn (II) and Ni (II) concentration. The relative recoveries of the method (expressed as the mean percentage between the amounts determined and the ones spiked) for the water samples were 95.0 −102.0% and 96.0–104.0% with the relative standard deviations (RSDs) of 2.3–2.8% and 2.4–2.9% for Mn (II) and Ni (II), respectively. These results indicate a good performance of this method for the determination of Mn (II) and Ni (II) in natural water samples.

3.10. *Comparison of the Proposed SPE Method with Other SPE Methods.* A comparison of the proposed SPE method with other SPE methods for the manganese and nickel extraction and determination from water samples is given in Table 5. In comparison with other reported methods, the proposed method has low LOD and good preconcentration factor. The method developed in this work is proposed as a suitable alternative to more expensive instruments for manganese and nickel determination at trace levels. This methodology is a reproducible, simple and low-cost technique, and does not require further instrumentation. These characteristics are of great interest for the routine laboratories in the trace analysis of metal ions.
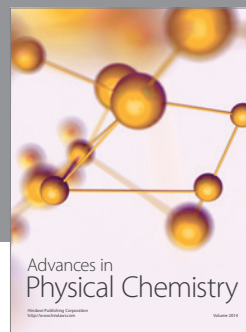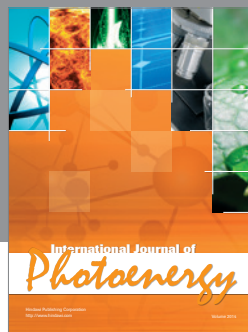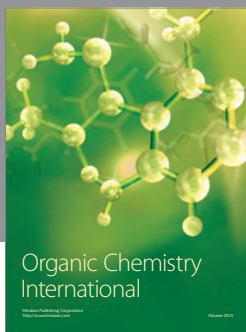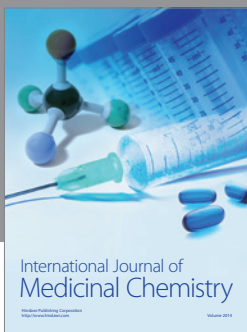
4. Conclusion

The work described in this paper shows the feasibility of the preconcentration of Mn (II) and Ni (II) species by the use of silica-gel minicolumn modified with diimine derivative Schiff base. The modified minicolumns are easy to prepare and the analyte are quickly adsorbed. A large volume of water sample (1000 mL) can be processed without break through and the preconcentrated metal ions can be easily desorbed with 5 mL of mixture of nitric acid 5 mol L^{-1} and methanol (1 : 1), resulting in a high-concentration factor (200 fold). The presented method can be easily applied for the preconcentration of Ni (II) and Mn (II) in natural water samples.

Acknowledgment

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