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Preconcentration of Nickel Using Chemically Modified Silica Nanoparticles

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Abstract

A procedure has been developed for the preconcentration of trace amounts of Ni(II) in different samples using 1-(2-pyridylazo)-2-naphthol modified SiO_2 nanoparticles as solid-phase extractant. Various parameters such as preconcentration factor, effect of pH, sample volume, shaking time, elution conditions and effects of interfering ions for the recovery of analyte have been optimized. The adsorption capacity of SiO_2-PAN nanoparticles has been found to be 42.81μmol g^{-1} at optimum pH. The detection limit (3σ) has been found to be 0.43 μg L^{-1}. The extractant showed rapid kinetic sorption. The adsorption equilibrium of Ni(II) on SiO_2-PAN nanoparticles was achieved within 10mins. Adsorbed Ni(II) was easily eluted with 5 mL of 6 mol L^{-1} hydrochloric acid. The maximum preconcentration factor has been found to be 60. The method has been applied for the determination of trace amounts of Ni(II) in water samples.

Keywords:

Chemically modified SiO_2-nanoparticles; Preconcentration; Separation; SiO_2-PAN nanoparticles

1. Introduction

Heavy metals contamination is recognized as a priority problem in environmental protection. Metal ions such as copper, lead, mercury, cadmium, cobalt etc, usually represent an environmental concern when present in uncontrolled and high concentrations. Metals are indispensable to the industrial, agricultural and technological advancement of any nation. The number of applications of metals for the commercial uses continue to grow with the developments in modern science and technology. Industrial processes and spent commercial products generate large quality of metallic waste products, which are discharged into the water or land-dump sites. Nickel is largely present in wastewater of electroplating, motor vehicle and aircraft industries. Acute nickel poisoning causes dizziness, head ache, nausea and vomiting, chest pain, dry cough and shortness of breathe rapid respiration and extreme weakness [1-6]. World Health Organization, WHO has suggested that the maximum amount of nickel in drinking water should be 0.1 mgL^{-1}. But in many electroplating effluent water it is high as 50 mgL^{-1}. The direct determination of metals in effluents or in saline matrices by atomic spectrophotometry such as flame or plasma techniques is difficult due to the nebulizers blockage, the high background, transport and chemical interferences which result in a decrease in precision and sensitivity. Therefore, separation and preconcentration methods have played a fundamental role in solving these problems.

The concept of extraction and preconcentration play important roles in many analytical procedures. Solvent extraction and solid phase extraction are arguably the most commonly executed forms of preconcentration and for many years they have dominated

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approaches to the enrichment of pesticides, drugs and trace metals. There are, however, physical difficulties associated with the use of solvent extraction for the enrichment of large numbers of samples and/or enrichment from large sample volumes. Solvent extraction requires vigorous agitation, to ensure complete partition of the analyte between two immiscible phases and this can only be achieved by the application of significant human or mechanical effort. In addition, there are increasing environmental and cost pressures to replace, or at the very least reduce, the volumes of solvents employed in analytical procedures. Many adsorption materials such as organic chelate resin, silica gel, activated carbon, activated alumina, zeolites and microcrystalline materials are commonly used as adsorbents [7-13]. Nowadays, nanometer materials have become more important owing to its special physical and chemical properties. 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. One of the specific properties of nanomaterials is that a high percent of atoms of the nanoparticle is on the surface. The surface atoms are unsaturated and can therefore bind with other atoms, possess high chemical activity. Nanoparticles exhibit intrinsic surface reactivity and high surface areas and can strongly chemisorb many substances. 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 [14-19]. In present work, chemically grafted SiO_2-PAN nanoparticles have been used for the preconcentration and separation of nickel prior to its determination by spectrophotometric method.

2. Experimental

2.1 Apparatus

Absorbance of Ni(II) was measured with UV-Vis Shimadzu-1700 spectrophotometer. The pH values were controlled by century Cp-901 digital pH meter. SEM micrographs were recorded on JEOL JEM 6100.

2.2 Reagents and standard solutions

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. The pH adjustments were made with hydrochloric acid or ammonia /ammonium chloride buffer. Stock solution of Ni(II) was prepared by dissolving spectral pure-grade chemicals nickel nitrate and diluted as and when required. The glassware was washed with chromic acid and soaked in 5% nitric acid overnight and then cleaned with double distilled water before use.

2.3. Modification Process

Silica nanoparticles were prepared by stober method [20]. Surface modification of SiO_2 nanometer particles were performed in a 250 mL flask. Nanometer SiO_2 (1 g) was dispersed into dry toluene (30 mL), and then 3-aminopropyltriethoxysilane (4 mL) was gradually added with continuous stirring. The mixture was refluxed for 6 h. The nanometer SiO_2-bound amino was filtered off, washed with toluene and ethanol and dried at 60°C for 3 h. The product was transferred into the flask, then 100 mL absolute ethanol dried were added followed by 20 mL formaldehyde, 2.5 mL concentrated hydrochloric acid and (1 g) 1-(2-pyridylazo)-2-naphthol and refluxed at 72 °C for 4 h. Reaction mixture was filtered under vaccum at 60 °C.

2.4 General procedure

Aliquots of sample solution containing 0.5µg Ni(II) was taken and pH 9.2 was adjusted with ammonia and ammonium chloride buffer. Then, 30 mg of SiO_2-PAN nanoparticles were added, and the mixture was shaken vigorously for 10mins to facilitate adsorption of metal ion onto the adsorbent. Ni(II) retained on the adsorbent was eluted with 6 mol L^{-1} hydrochloric acid, and the elution was neutralized with 2 mol L^{-1} sodium hydroxide. Then, these metal ions were filtered and were determined by standard spectrophotometric method [21].

3. Results and discussion

3.1. Scanning Electron Microscopy

The average diameter of the nanoparticles SiO_2 and SiO_2 -PAN was 100 nm, and 2 µm confirmed by Scanning Electron Microscopy respectively. Fig. 1 and 2 reveals the average size of SiO_2 nanoparticle and SiO_2 -PAN nanoparticles respectively.

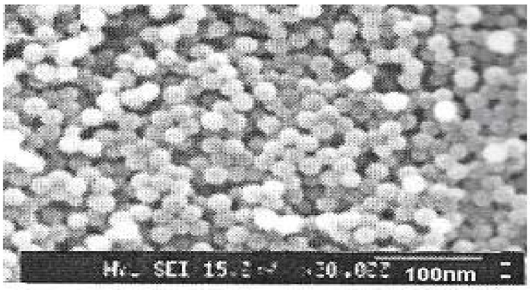

Fig.1. SEM micrograph of SiO_2 nanoparticle.

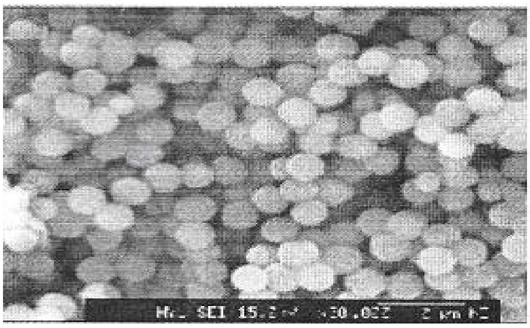

Fig .2. SEM micrograph of SiO_2-PAN nanoparticle.

3.2. Effect of pH on enrichment recovery

The adsorption of Ni(II) on SiO_2-PAN nanoparticles was studied at different pH value (2.0 to 11.0) following the recommended procedure. The results of effect of pH on the recoveries of the Ni(II) was shown in Fig.3. It can be seen that a quantitative recovery (≥95%) was found for Ni(II) in the pH range of 8.0-11.0. 9.2 pH was selected for further analysis.

3.3. Effect of eluent concentration and volume

Elution of Ni(II) from SiO_2-PAN nanoparticles was investigated by using various concentrations of hydrochloric acid. It can be seen that quantitative recoveries (≥95%) of Ni(II) can be obtained using 5 mL of 6 mol L^{-1} HCl as eluent. Therefore, 5 mL of 6 mol L^{-1} was used as eluent in subsequent experiments. The results of effect of eluent concentration and volume are given in Table 1 and Table 2.

3.4. Effect of nanometer SiO_2-PAN amount

To test the effect of amount of extractant on quantitative retention of analyte, different amount (5-40 mg) of SiO_2-PAN nanoparticles were added into the solution following the experimental method. Quantitative extraction of the Ni(II) (≥ 95%) was obtained in the range of 25-40 mg of SiO_2-PAN nanoparticles. 30 mg of nanometer SiO_2-PAN as extractant was found to be sufficient for further studies. The results are shown in Fig. 4.

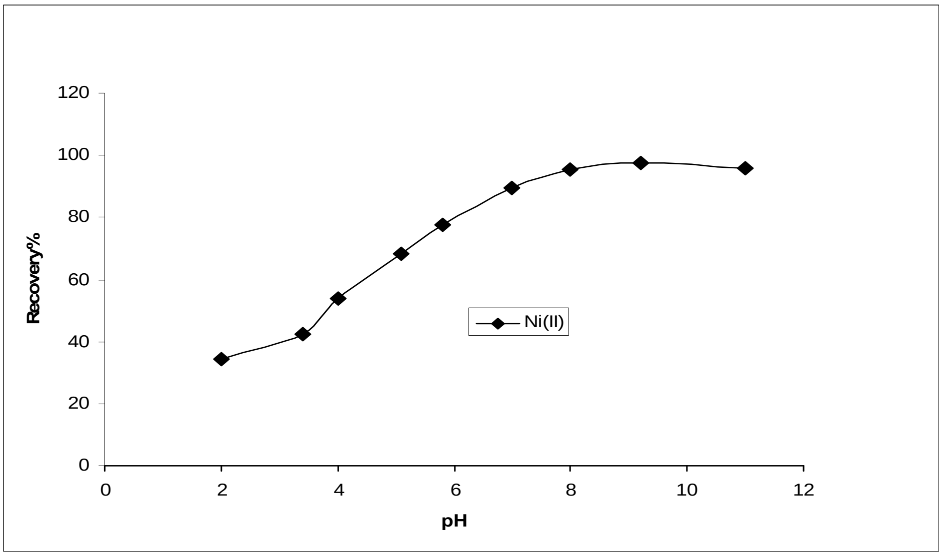

Fig.3. Effect of pH on recovery%.

Table1. Effect of concentration of HCl solution on elution of Ni(II) (n=5)

Concentration of eluent (mol L^{-1})	2.0	4.0	6.0	8.0	10.0
Recovery (%)	35.60	84.50	96.42	80.64	50.80

Table 2. Effect of volume of HCl solution on elution of Ni(II) (n=5)

Volume of elution (mL)	2.0	4.0	5.0	6.0	8.0	10.0
Recovery (%)	40.57	75.09	96.51	89.71	76.41	54.31

3.5. Effect of shaking time

The adsorption of Ni(II) on 30 mg of SiO_2-PAN nanoparticles was studied for different shaking time (2-30 mins). The results indicated that within 10 mins the extraction percentage of Ni(II) ≥95% was achieved. The results are shown in Fig. 5.

3.6. Adsorption capacity (Q_S)

A breakthrough curve was obtained by plotting the concentration (mgL^{-1}) vs. the μmol of Ni(II) adsorbed per gram. From the breakthrough curve the amount of modified SiO_2-PAN nanoparticles for Ni(II) was found to be 42.81 μmol g^{-1} at pH 9.2. The results are shown in Fig. 6.

3.7. 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 Ni(II) was also investigated. For this purpose 20, 50, 100, 150, 200, 250, 300, 400 and 500 mL of the sample solutions containing 1.0 μg Ni(II) was shaken, quantitative recoveries (≥95%) were obtained for sample volume of ≤300mL for Ni(II). The results are given in Fig. 7.

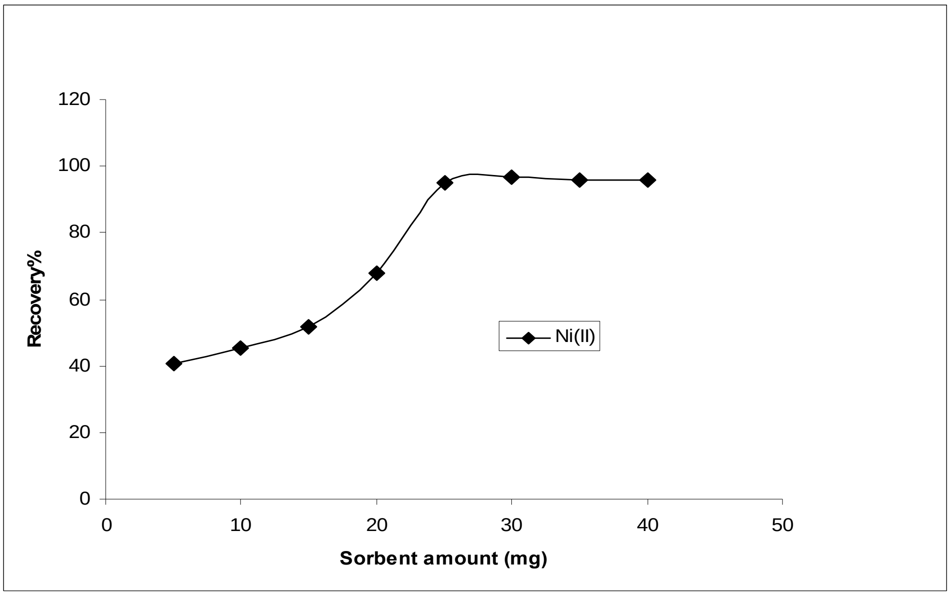

Fig.4. Effect of sorbent amount on recovery%.

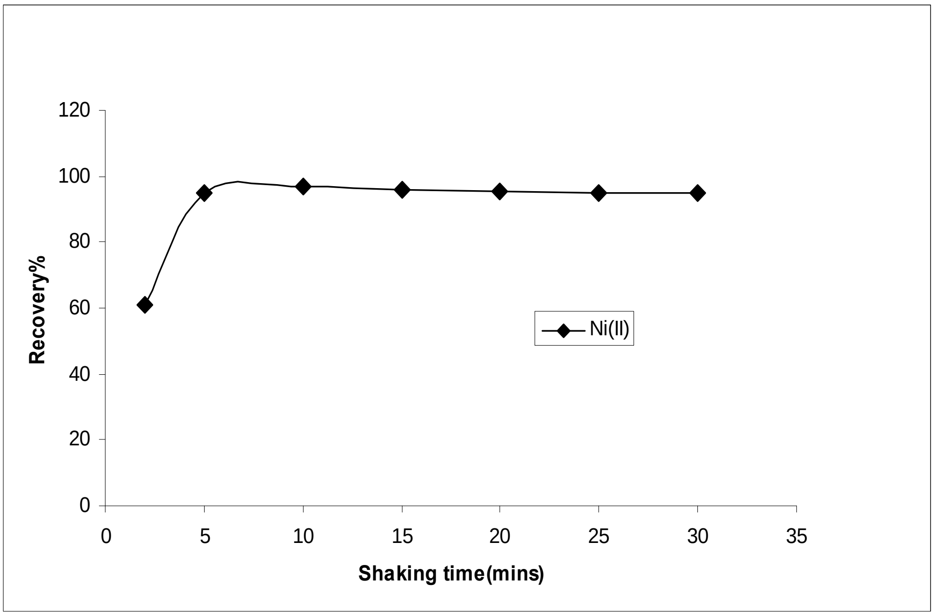

Fig.5. Effect of shaking time on recovery %.

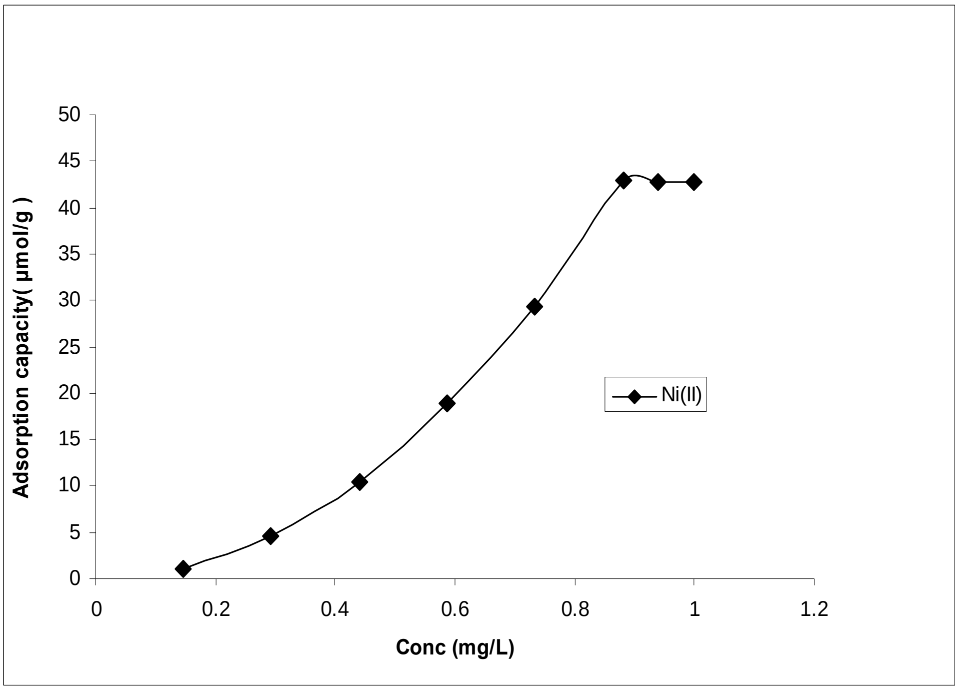

Fig. 6. Adsorption capacity of Ni(II) on nanometer SiO_2-PAN.

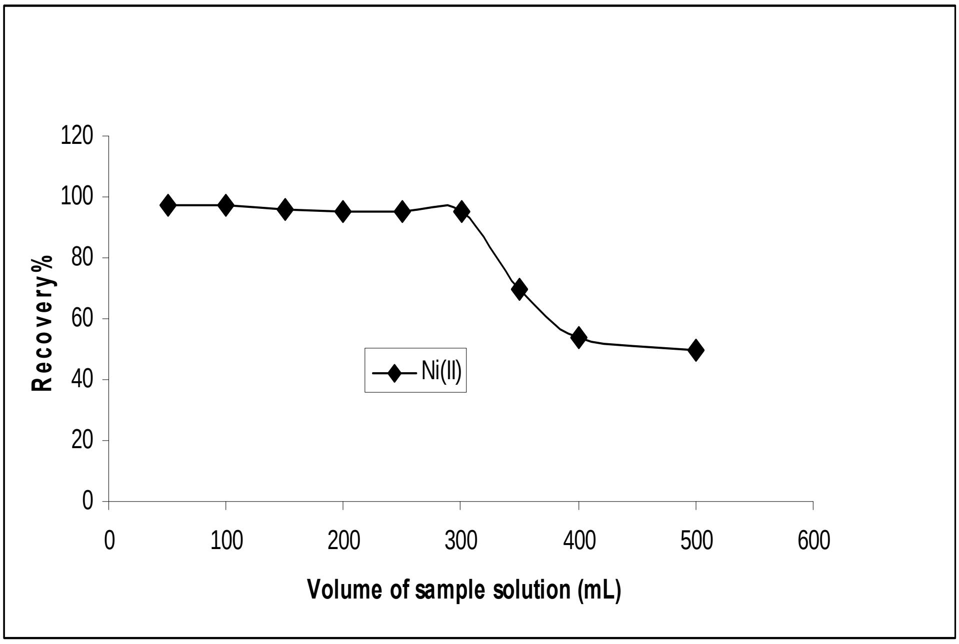

Fig.7. Effect of volume of sample solution on recovery %.

3.8. Effect of coexisting ions

The effect of common coexisting ions on the sorption of Ni (II) was investigated. In these experiments, solutions 5 µg mL^{-1} of Ni(II) that contains the added interfering ion were analyzed according to the recommended procedure. The tolerance of the coexisting ions, defined as the largest amount making the recoveries of Ni(II) less than 90%. The tolerance limits were 300, 40, 40, 200, 20, 100, 80, 90, 60, 90, 60 and 60 mg L^{-1} for Ca^{2+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, Al^{3+}, Fe^{2+}, Cu^{2+}, V^{5+}, Bi^{3+}, Pb^{2+}, Co^{3+}, respectively. Thus, the presence of major cations has no obvious influence on the determination under the optimum conditions. This is due to low adsorbing capacity on SiO_2-PAN nanoparticles and because K^+ and Na^+ were not adsorbed by SiO_2-PAN nanoparticles, thousand-fold excesses of K^+, Na^+ had no effect on the preconcentration and determination of analyte. Apparently, the tolerance limits of foreign ions are higher than the concentrations of those ions in the other samples. Besides, a lot of anions NO_3^-, SO_4^{2-}, $S_2O_3^{2-}$, $C_2O_4^{2-}$, $H_2PO_4^-$, I^-, CO_3^{2-} and Cl^- etc did not interfere in preconcentration and determination of Ni(II).

3.9. Analytical precision and detection limit

Under the selected conditions, three portions of Ni(II) standard solutions was enriched and analyzed simultaneously following the experimental method. The relative standard deviation (RSD) of the method was 4.1% for the determination of 5µg Ni(II) in 100 mL water samples. The detection limit of this method for Ni(II) was 0.43 µg L^{-1}.

4. Applications

The developed method has been applied for the determination of trace Ni(II) in tap water and mineral water. The results are given in Table 3.

Table 3. Analytical recovery of Ni(II) added to some water samples (n=5).

Samples	Added (µg/L)	Found (%) (µg/L)	Recovery
Tap water	0.0	unfound	----
	10.0	9.79	97.90
	20.0	19.59	97.95
Mineral water	0.0	unfound	----
	10.0	9.81	98.10
	20.0	19.65	98.25

5. Conclusions

1-(2-pyridylazo)-2-naphthol-anchored silica nanoparticles were prepared and used as solid sorbent for preconcentration and separation of trace Ni(II) prior to their determination. These analyte can be easily screened at µgmL^{-1} level with preconcentration times of 10mins and preconcentration factor of 60 for Ni(II).

The method can be used as screening to estimate the total concentration of Ni(II) present in a large number of samples and thus avoiding the continuous use of expensive instrumentation in routine analysis. 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 water samples. The results of determination have been found to be accurate and reproducible.

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