Chemically Modified Submicron Silica Particulate Extractants for Preconcentration of Mercury(II)

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A new analytical method using 1-(2-pyridylazo)-2-naphthol modified SiO_2 nanoparticles as solid-phase extractant has been developed for the preconcentration of trace amounts of mercury(II) in different water samples. Conditions of the analysis such as preconcentration time, effect of pH, sample volumes, shaking time, elution conditions and effects of interfering ions for the recovery of analyte were investigated. The adsorption capacity of nanometer SiO_2-PAN was found to be 260 μmolg^{-1} at optimum pH and the detection limit (3σ) was 0.48 μgL^{-1}. The extractant showed rapid kinetic sorption. The adsorption equilibrium of mercury(II) on nanometer SiO_2-PAN was achieved just in 5 mins. Adsorbed mercury(II) was easily eluted with 5 mL of 6 M hydrochloric acid. The maximum preconcentration factor was 50. The method was applied for the determination of trace amounts of mercury(II) in various water samples and industrial effluents.

Key Words : Chemically modified SiO_2-nanoparticles, 1-(2-Pyridylazo)-2-naphthol, Preconcentration and separation

Introduction

In recent years, the toxicity and effects of trace elements to the danger of public health and environment have attracted increasing attention in the fields of pollution and nutrition. Mercury and its organometallic species are considered to be highly toxic to the environment.[1-5] WHO recommends a limit of 1 μgL^{-1} of mercury(II) in drinking water. Direct determination of mercury at trace levels from natural water by conventional method is limited on account of its low concentration and matrix interferences. In trace analysis, therefore preconcentration or separation technique is frequently necessary to improve the detection limit and selectivity. It becomes necessary to develop an accurate selective and sensitive method for quantitative determination of mercury(II) in the environmental samples. One of the most important objectives for analytical chemists is metal quantification at trace level (< μgL^{-1}) or ngmL^{-1}. Despite recent progress in instrumental techniques and increases in the selectivity and sensitivity of analytical techniques, direct determination of trace elements in sample is still difficult. Therefore, preconcentration and selective separation of trace elements is very important.

The most frequently used method for preconcentration of mercury(II) from natural waters is solvent phase extraction,[6-8] ion-exchange resins,[9] resin chelation,[10] coprecipitation[11] and solid phase extraction.[12] Solid phase extraction with immobilized organic compounds is attracting great interest because of its high enrichment capability and operation simplicity. Nowadays, nanometer materials have become more important owing to its special physical and chemical propertities. Nanoparticles are cluster of atoms or molecules of metal and oxide ranging in the size from 5-5000 nm, falling between single atom or molecule and bulk materials. One of the properties of nanoparticles is that most of atoms are on the surface. The surface atoms are unsaturated and therefore can bind other atoms that have a high chemical activity. Investigations of surface chemistry of highly dispersed oxides *e.g.* TiO_2,[17-19] Al_2O_3,[20,21] ZrO_2,[22] Chitosan[23] and CeO_2[24,25] indicate that these materials have a very high adsorption capacity and give promising results when used for trace metal and analysis of different types of solution samples.

In this work, nanometer SiO_2 was modified chemically by 1-(2-pyridylazo)-2-naphthol (PAN) as a solid-phase extractant. The adsorption behavior of analyte on nanometer SiO_2-PAN has been investigated in detail and the conditions have been optimized for the separation and preconcentration of mercury in different samples. The proposed method has been applied for preconcentration of trace mercury(II) from sample solutions and then determined by standard spectrophotometric method. Analytical precision and accuracy of the proposed method was checked and found to be quite satisfactory and the method was convenient to use.

Experimental

Instruments and apparatus. Absorbance of mercury(II) was measured with UV-VIS Shimadzu-1700 spectrophotometer. The pH values were controlled by century Cp-901 digital pH meter. Infrared spectra was recored on a Perkin Elmer FT-IR apparatus.

Reagents and standards. Unless otherwise stated, all reagents used were of analytical grade and all 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 SiO_2 was synthesized

according to the method reported.[26] The pH adjustments were made with hydrochloric acid or ammonia and pH was maintained with acetic acid/sodium acetate buffer. Stock solution of mercury(II) was prepared, standardized before use 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.

Sample preparation. Tap water samples taken from research laboratory were analyzed without pretreatment. The pH value was adjusted to 4 with 0.1 M hydrochloric acid or 0.1 M ammonium hydroxide prior to use. Industrial effluents were collected from Unitech Thermometers industry from (Delhi) and these were filtered through a 0.2 μm cellulose nitrate membrane filter.

Modification process. Surface modification of SiO_2 nanoparticles 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 hours. The silylated nanometer SiO_2 was filtered off, washed with toluene and ethanol and dried at 60 °C for 3 hours. The product was transferred into the flask, and then 100 mL absolute ethanol was added followed by 20 mL formaldehyde, 2.5 mL concentrated hydrochloric acid and 1g PAN and refluxed at 72°C for 4 hours. Reaction mixture was filtered under vaccum.

General procedure. A portion of standard or sample solution containing mercury(II) was transferred into a 10 mL beaker and pH was adjusted to the desired value and the final volume was made upto to 10 mL with double distilled deionized water. 50 mg of SiO_2-PAN particles were added, and the mixture was shaken vigorously for 5 mins to facilitate adsorption of mercury(II) onto the adsorbent. After this the solution was filtered through cellulose nitrate membrane filter. The concentration of mercury(II) in the solution was determined by standard spectrophotometric method. Mercury(II) retained on the adsorbent was eluted with 6 M hydrochloric acid, and the elution was neutralized with 2 M sodium hydroxide solution. It was filtered again, and mercury(II) in the filtrate was determined by spectrophotometric method.

Results and Discussion

SEM. The average diameter of the nanoparticles SiO_2, SiO_2-APTES and SiO_2-PAN was 100 nm, 1 μm and 2 μm confirmed by Scanning Electron Microscopy. Figure 1, 2 and 3 reveals the average size of SiO_2 nanoparticle, SiO_2-APTES and SiO_2-PAN respectively.

FT-IR spectrum. The chemical grafting of 1-(2-pyridylazo)-2-naphthol (PAN) on the surface of nanometer SiO_2 was confirmed by FT-IR spectrum. Figure 4 shows the FT-IR spectra of PAN, nano-SiO_2-PAN, nano-SiO_2-APTES and nano-SiO_2. Figure 4(a) reveals that main absorption peaks of nanometer SiO_2 (3448.0, 1642.5, 1404, 1070.2, 964.2, 798.8 cm^{-1}) are in agreement with standard spectrum of SiO_2.[27]

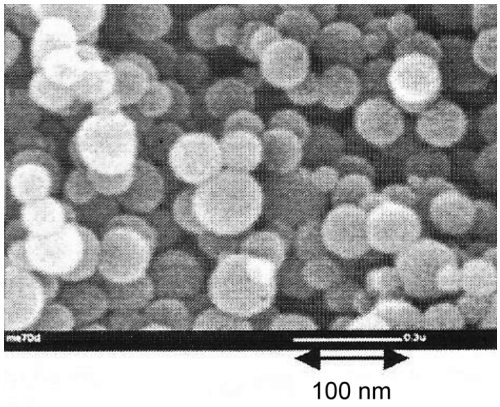

Figure 1. SEM micrograph of SiO_2 nanoparticles.

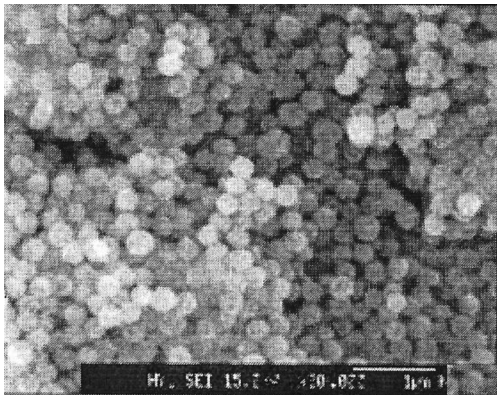

Figure 2. SEM micrograph of SiO_2-APTES nanoparticles.

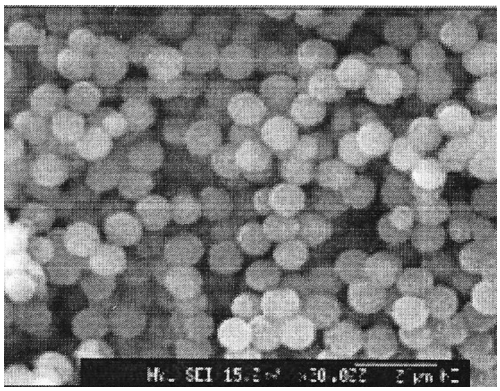

Figure 3. SEM micrograph of SiO_2-PAN nanoparticle.

Many new peaks appeared in Figure 4(b) which are assigned as follows: the peak at 1683.5 cm^{-1} is due to N=N stretching vibration of 1-(2-pyridylazo)-2-naphthol, the peaks of C=C stretching vibration for the benzenoid and pyridyl unit in 1-(2-pyridylazo)-2-naphthol occurs at 1590, 1540, 1500 and 695.9 cm^{-1}, the peak of 1381.6 cm^{-1} is due to CH_2 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. Figure 4(c) reveals that C-H stretching at 2907.2 cm^{-1}, NH_2 peak at 1641.3 cm^{-1} and C-O stretching at 1093.5 cm^{-1}. The above experimental results suggest that nanometer SiO_2 has been

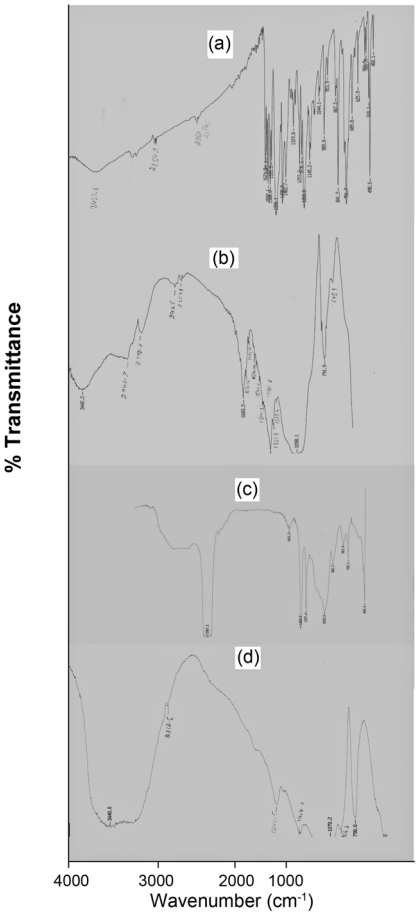

Figure 4. FTIR spectra (a) PAN (b) nanometer SiO_2-PAN (c) nanometer SiO_2-APTES (d) nanometer SiO_2.

successfully modified by 1-(2-pyridylazo)-2-naphthol.

Effect of pH on enrichment recovery. The adsorption of mercury(II) on nanometer SiO_2-PAN was studied at different pH values in the range (1.0-8.0) following the recommended procedure. The result shows quantitative extraction (> 95%) in the pH range of 4.0-8.0. In order to avoid hydrolysis at higher pH values, pH 4 was selected as the enrichment acidity for subsequent experiments. The adsorption of other metal ions on nanometer SiO_2 and nanometer SiO_2-PAN including Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Be(II), Cd(II), Hg(II), Pb(II), K(I), Na(I), Ca(II), Mg(II) and Al(III) ions were also studied in range of pH 1.0-8.0. The basic disadvantage of nanometer SiO_2 was lack of selectivity. For nanometer SiO_2-PAN, 1.0 mgL^{-1} Be(II), K(I), Na(I), Ca(II), Mg(II) and Al(III) were not enriched at pH 4, the extraction percentage of 1.0 mgL^{-1} Mn(II), Zn(II), Cu(II) and Cd(II) ions were only 10-15% and Co(II), Pb(II), and Ni(II) which were adsorbed on nanometer SiO_2-PAN reached 25-55% at pH 4, but they did not interfere with enrichment or determination of mercury(II). Retention is highly dependent on sample pH with quantitative retention requiring pH- values over 7.5-8, as under acidic conditions silanol groups are protonated and the ion-exchange capacity of the silica gel is greatly reduced or even reduced to zero at low pHs. PAN which was immobilized on the surface of

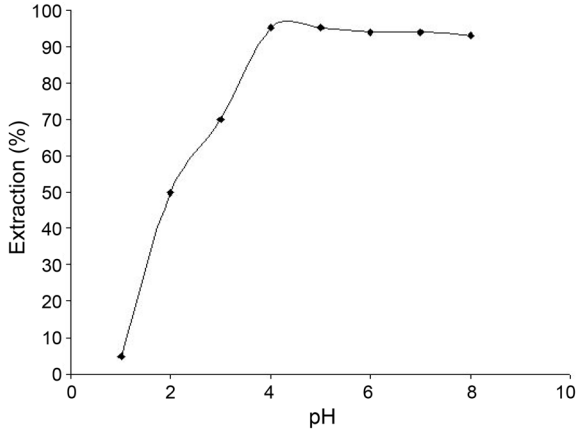

Figure 5. Effect of pH on analyte extraction percentage; mercury(II); 1.0 mgL^{-1}.

nanometer SiO_2 changed its surface structure, and made it could rapidly adsorb metal ion even at relatively low pH values.[29] These experiments show that nanometer SiO_2-PAN offers higher selectivity for mercury(II) adsorption than untreated nanometer SiO_2. The results are shown in Figure 5.

Effect of eluent concentration and volume. Since the adsorption of mercury(II) on nanometer SiO_2-PAN at pH < 1 is negligible, this means elution will be favored in acidic solution. So, various concentration of hydrochloric acid (10 mL) was studied for desorption of retained mercury(II). But it was found that nanometer SiO_2-PAN gradually presented good dispersion in hydrochloric acid solution when the concentration of hydrochloric acid solution increased. Nanometer SiO_2-PAN which was dispersed in eluent could not be removed completely through conventional centrifuge or filter. In order to resolve this problem, the elution was neutralized to pH 1.0. Then it was filtered, and mercury(II) in the filtrate was determined by standard spectrophotometric method.[28] Quantitative recovery of mercury(II) was obtained with 5 mL of 6.0 M hydrochloric acid. The effect of the eluent volume on the recovery of mercury(II) was also evaluated. The results of effect of eluent concentration and volume are given in Table 1 and Table 2 respectively.

Effect of nanometer SiO_2-PAN amount. To test the

Table 1. Effect of concentration of eluent (HCl) solution on elution of mercury(II)

Concentration of eluent (mol/L)	1	2	4	6	8	10
Recovery (%) (n = 3)	54	67	88	99	99.0	95.33

Table 2. Effect of volume of HCl solution on elution of mercury(II)

Volume of eluent (mL)	2	4	5	6	8	10
Recovery (%) (n = 3)	82	99	99.7	100.8	92.2	90.2

The concentration of mercury(II) was 10 μgL^{-1}; pH = 4

effect of amount of extractant on quantitative retention of analyte, different amounts (10-100 mg) of nanometer SiO_2-PAN were added into the solution following the experimental method. Quantitative extraction of the mercury(II) was obtained in the range of 25-75 mg of nanometer SiO_2-PAN. Quantitative retention was not obtained with amounts of extractant smaller than 50 mg or larger than 75 mg. Extractor amount larger than 100 mg may prevent the elution of the retained mercury(II). 50 mg of nanometer SiO_2-PAN as extractant was found to be sufficient for further studies.

Effect of shaking time. The adsorption of mercury(II) on 50 mg of nanometer SiO_2-PAN was studied for different shaking time (2-15 mins). The results indicated that within 5 mins the extraction percentage of mercury(II) greater than > 95% was achieved. Thus, the adsorption of mercury(II) on nanometer SiO_2-PAN was found to be quite fast. This may be due to the fact that the surface atoms of nanometer SiO_2 are unsaturated and tend to bind with other atoms that feature high chemical activity. The surface of nanometer SiO_2 is characterized by the presence of silanol groups, which are known to be weak ion-exchangers, causing low interaction, binding and extraction of ionic species.[30] 1-(2-pyridylazo)-2-naphthol (PAN) which was chemically grafted on the surface of nanometer SiO_2 changed its surface structure and this resulted into rapid adsorption of metal ion even at relatively low pH values.

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 detail study of nanometer SiO_2-PAN indicated a much higher adsorption capacity[31] as compared to that of nano-SiO_2. A breakthrough curve was obtained by plotting the concentration (mgL^{-1}) *vs*. the μmol of mercury(II) adsorbed per gram. The breakthrough curve of Figure 6, the amount of modified nanometer SiO_2-PAN for mercury(II) was found to be 260 $\mu molg^{-1}$.

Effect of the 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 metal ions was also investigated. For this purpose, 20, 50, 100, 150, 200, 250, 300 and 400 mL of the sample solutions containing 2 μg mercury(II) was shaken. Breakthrough volume is the maximum sample volume from which 100% recovery can be achieved. The breakthrough volume depends on the sample volume, the type and quantity of sorbent, hydrophobicity and ionizability of the analyte and pH. The breakthrough volume for a specific mass of the sorbent (50 mg) has been established by loading variable-volume sample of a constant concentration. The breakthrough volume was 250 mL in the determination of mercury(II). As shown in Figure 7, quantitative recoveries (>95%) were obtained for sample volume of ≤ 250 mL for mercury(II) from sample solution.

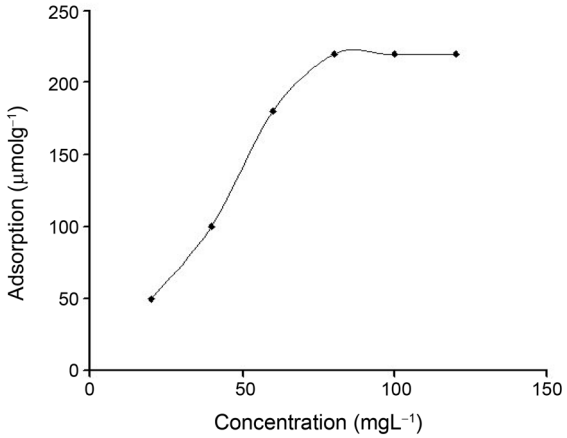

Figure 6. Adsorption capacity of mercury(II) on nanometer SiO_2-PAN; pH 4; Sample volume 5 mL.

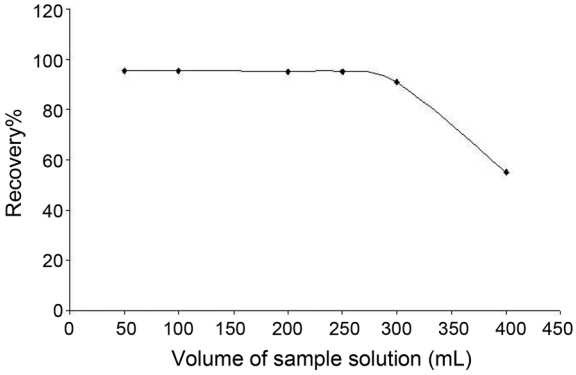

Figure 7. Effect of sample volume on analyte recovery; pH 4; mercury(II); 2.0 μg.

Effect of coexisting ions. The effect of common coexisting ions on the sorption of mercury(II) was investigated.[32] In these experiments, solutions 10 μgL^{-1} of mercury(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 mercury(II) less than 90%. The tolerance limits were 300, 40, 40, 200, 20, 100, 80, 90, 60, 90, 10, and 200 mgL^{-1} for Ca^{2+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, Al^{3+}, Fe^{2+}, Cu^{2+}, V^{5+}, Bi^{3+}, Pb^{2+}, Co^{2+}, Ni^{2+} 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 nanometer SiO_2-PAN and because K^+ and Na^+ were not adsorbed by nanometer SiO_2-PAN, 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 NO_3^-, SO_4^{2-}, $S_2O_3^{2-}$, ClO_4^-, $H_2PO_4^-$, I^-, CO_3^{2-} and Cl^- etc did not interfere with enrichment or the determination of mercury(II).

Analytical precision and detection limits. Under the optimized conditions, three portions of mercury(II) standard solutions were enriched and analyzed simultaneously by the general procedure. The relative standard deviation (RSD) of the method was 1.25%, indicating that the method has good precision for the analysis of trace mercury(II) from solution samples and the detection limits (3s) for mercury(II) was 0.48 μgL^{-1} ($n = 3$).[33]

Applications. The developed method has been applied for

Table 3. Analytical results of samples

Samples	Added	Results	Recovery (%) (n = 3)
Tap Water	0	unfound	–
	0.5	0.45	90
	1.0	0.92	92
	2.0	2.01	100.5
Industrial effluent	0	0.80	–
	0.5	1.30	100
	1.0	1.84	105
	2.0	2.80	100

Table 4. Figure of merit of comparable methods for the determination of mercury(II) by Solid-phase extraction

Support	Reagent	LOD (μg/L)	Ref
Silica Gel	3-(-2-thioimidazolyl)propyl	5.0	34
Silica Gel	Dithioacetal	10.0	35
Silica Gel	3-mercaptoimidazole	5.0	36
Silica Gel	2-amino-1,3,4-thiadiazole	5.0	37
Silica Gel	Xylenol orange	10.0	38
Silica Gel	Methylthiosalicylate	10.0	39
Silica-APTES nanoparticles	PAN	0.48	this work

the determination of trace mercury(II) in the tap water and industrial effluents. For analysis, 200 mL of sample was extracted following the method described above. The results are given in the Table 3.

Conclusions

1-(2-Pyridylazo)-2-naphthol modified nanometer SiO_2 was prepared and used as a solid sorbent to preconcentrate and separate trace mercury(II) prior to their determination by standard method. In this study, a simple, rapid, accurate, selective and reliable method for the enrichment of trace level of mercury(II) was developed using nanosized SiO_2-PAN as solid phase extractant which showed great adsorption capacity and excellent selectivity. The preparation of nanometer SiO_2-PAN is relatively simple and rapid. This newly developed nanosized extractant has been successfully applied to preconcentrate trace mercury(II) in tap water and industrial effluents. The method is a green approach as it does not require the use of any toxic solvents. Comparative information from some studies on preconcentration of mercury(II) by various methods for figure of merits is given in Table 4. The proposed method developed using SiO_2-PAN nanoparticle had a relatively high LOD compared to other methods reported in Table 4.

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