Sorption and Preconcentration of Lead on Silica Nanoparticles Modified with Resacetophenone

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Abstract: The silica-resacetophenone (SiO₂-RATP) nanoparticles were used as a new sorbent for extraction of trace amounts of Pb(II) by batch technique. Conditions of the analysis such as preconcentration factor, effect of pH, sample volume, shaking time, elution conditions and effects of interfering ions for the recovery of analyte were investigated. The adsorption capacity of nanometer SiO₂-RATP was found to be 167.24 µmol/g at optimum pH and the detection limit (3σ) was 0.58 µg/L. The adsorption equilibrium of Pb(II) on nanometer SiO₂-RATP was achieved in 20 min. Adsorbed Pb(II) was easily eluted with 5 mL of 0.5 M hydrochloric acid. The maximum preconcentration factor was 60. The method was applied for the determination of trace amounts of Pb(II) in various natural water rivers.

Keywords: Chemically modified SiO₂-nanoparticles, RATP, Preconcentration and Separation, Resacetophenone.

Introduction

Heavy metal ions contamination is recognized as a priority problem in environmental protection because these represent an environmental concern when present in uncontrolled and high concentration. Lead is considered as non-essential and highly toxic element with a series of cumulative effect. Its toxicity is comparable of any other metallic element. It is toxic to the human biosystem, and is among the common global pollutants arising from increasing industrialization. So, there is need to determine lead up to micro levels¹⁻⁵. Despite the selectivity and sensitivity of analytical techniques, there is crucial need for the preconcentration of trace elements before their analysis due to their frequent low concentrations in numerous samples⁶⁻¹². Nowadays, nanometer materials have become more important owing to its special physical and chemical properties. Nanoparticles exhibit intrinsic surface activity due to high surface areas and can strongly chemisorb many chemical 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 areas¹³⁻¹⁴. Nanoparticles such as TiO_2 ¹⁵⁻¹⁶, Al_2O_3 ¹⁷ and ZrO_2 ¹⁸⁻¹⁹ have been used for the preconcentration of many metal ions and give promising results when used for trace element analysis of different samples. In present work, chemically grafted SiO_2 -RATP nanoparticles have been used for the sorption and preconcentration of lead prior to their determination by spectrophotometric method. These chemically modified SiO_2 -RATP nanoparticles are characterized by Fourier Transform Infrared Spectroscopy (FT-IR).

Experimental

Absorbance of Pb(II) was measured with UV-Vis Shimadzu-1700 spectrophotometer. The pH values were controlled by century Cp901 digital pH meter.

Reagents and standard solutions

Unless otherwise stated, all reagents used were of analytical reagent grade and all solutions were prepared with double distilled water. The 3-aminopropyltriethoxysilane of GR grade was supplied by Acros Organics (USA). Resacetophenone (RATP) was obtained from Merck (Mumbai). Nanometer SiO_2 and modified SiO_2 -RATP was synthesized according to the method reported²⁰⁻²¹.

Sample preparation

Different water samples (River water) were analyzed without pretreatment. The pH was adjusted to 7.0 by using 0.2 M disodium tetraborate/boric acid buffer prior to use.

General procedure

Aliquots of sample solutions containing the analytes of interest were prepared and pH value was adjusted to the selected value with disodium tetraborate/boric acid buffer (0.2 M). Then, 20 mg of SiO_2 -RATP nanoparticles were added, and the mixture was shaken vigorously for 20 min to facilitate sorption of metal ion onto the adsorbent. Pb(II) sorbed on the sorbent was eluted with 5 mL of 0.5 M hydrochloric acid to get free metal ions, the solution was neutralized with 2 M sodium hydroxide and were determined by standard spectrophotometric method.

Results and Discussion

FT-IR spectrum analysis

The chemical grafting of resacetophenone the surface of nanometer SiO_2 was confirmed by FT-IR spectrum. FT-IR spectra of resacetophenone, nanometer- SiO_2 , nanometer - SiO_2 -RATP, respectively (Figure 1). It 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 spectrum¹⁷ of SiO_2 . The FT-IR spectrum of nanometer - SiO_2 -RATP, exhibits a band at 1613.9 cm^{-1} which appears to be contributed to by C=N stretching. The phenyl vibrations appears at 1493.9 cm^{-1} and 1373 cm^{-1} . The above experimental results suggest that nanometer SiO_2 has been successfully modified by resacetophenone.

Effect of pH on enrichment recovery

The adsorption of Pb(II) on nanometer SiO_2 -RATP was studied at different pH value (3.4 - 10.0) following the recommended procedure. The results of effect of pH on the recoveries of the metal ions are given in (Figure 2). A quantitative recovery ($\geq 95\%$) was found for Pb(II) in the pH range of 7.0-10.0.

Figure 1. FTIR spectra (a) Resacetophenone (b) Nanometer SiO_2 - Resacetophenone (c) Nanometer SiO_2 – APTES (d) Nanometer SiO_2 .

Figure 2. Effect of pH on analyte recovery.

Effect of eluent concentration and volume

Elution of Pb(II) from nanometer SiO₂-RATP sorbent was investigated by using different concentrations of hydrochloric acid and found quantitative recoveries ($\geq 95\%$) of Pb(II) could be obtained using 5 mL of 0.5 M hydrochloric acid as eluent. The results of effect of eluent concentration and volume are given in Table 1 and Table 2.

Table 1. Effect of concentration of HCl solution on elution of Pb(II) (n=3).

Concentration of eluent M	0.2	0.5	1.0	2.0	4.0	6.0
Recovery, %	57.76	99.46	72.68	43.61	33.28	22.18

Table 2. Effect of volume of HCl solution on elution of Pb(II) (n=3).

Volume of eluent, mL	2.0	4.0	5.0	6.0	7.0	10.0
Recovery, %	45.90	64.26	99.08	95.25	76.51	57.38

Effect of nanometer SiO₂-RATP amount

To optimize the amount of sorbent on quantitative retention of analyte, different amounts (10-60 mg) of SiO₂-RATP nanoparticles were added into the solution following and the experiment was performed. Quantitative extraction of the Pb(II) $\geq 95\%$ was obtained in the range of 20-35 mg of nanometer SiO₂-RATP. 20 mg of sorbent was found to be sufficient for further studies.

Effect of shaking time

The sorption of Pb(II) on 20 mg of RATP modified silica nanoparticles were studied for different shaking time (5-30 min). The results indicated that within 20 min the quantitative extraction of Pb(II) was $\geq 95\%$.

Adsorption capacity (Q_s)

The adsorption capacity²² is an important factor as it determines how much sorbent is quantitatively required to concentrate the analytes from a given solution. A breakthrough curve was obtained by plotting the concentration (mg/L) vs. the μmol of Pb(II) sorbed per gram. From the breakthrough curve the amount of SiO₂-RATP nanoparticles for Pb(II) was found to be 167.24 $\mu\text{mol/g}$ at pH 7.0 respectively. The results are given in Figure 3.

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 Pb(II) was also investigated.

For this purpose 50, 100, 150, 200, 250, 300, 350, 400, 450 and 500 mL of the sample solutions containing $1.0 \mu\text{g Pb(II)}$ was shaken, quantitative recoveries ($\geq 95\%$) were obtained for sample volume of ≤ 300 mL for Pb(II). The results are given in Figure 4.

Figure 3. Adsorption capacity of Pb(II) on nanometer SiO_2 -RATP.

Figure 4. Effect of sample volume on analyte recovery.

Effect of coexisting ions

The effect of common coexisting ions on the sorption of Pb(II) was investigated. In these experiments, a solution of $2.0 \mu\text{g/mL}$ of Pb(II) that contains the added interfering ion was analyzed according to the recommended procedure. The tolerance limit (mg/L) for anions such Cl^- , Br^- , SO_4^{2-} , PO_4^{3-} , NO_3^- , and EDTA The tolerance limits of these anions in mg/mL were 0.003, 0.02, 0.07, 0.005, 0.05, and 0.02 respectively. The tolerance limits in mg/mL for Ca(II), Mg(II), Cu(II), Co(II), Ni(II), Cr(III), Mn(II), Zn(II) and Cd(II) were 0.05, 0.10, 0.09, 0.010, 0.010, 0.010, 0.08, 0.075, 0.011 and 0.07 respectively.

Analytical precision and detection limit

Under the selected conditions, three portions of Pb(II) standard solutions was enriched and analyzed simultaneously following the experimental method. The relative standard deviation

(RSD) of the method was 3.8% for the determination of 5.0 µg Pb(II) in 100 mL river water samples. The detection limit of this method for Pb(II) was 0.58 µg/L.

Applications

The developed method has been applied for the determination of trace Pb(II) in river water. For analysis, 200 mL of sample was extracted following the method described above. The results are given in the Table 3.

Table 3. Analytical recovery of Pb(II) added to natural water samples.

Samples	Added, µg/L	Found, µg/L	Recovery, %
Ganga river (Delhi)	0.0	19.28	---
	5.0	23.88	97.95
	10.0	28.93	98.23
Yammuna river (Delhi)	0.0	17.45	---
	5.0	20.96	98.42
	10.0	27.62	96.39

Conclusion

Resacetophenone anchored silica nanoparticles were prepared and used as solid sorbent for preconcentration and separation of trace Pb(II) prior to their determination. These analytes can be easily screened at µg/mL level with preconcentration times of 20 min and preconcentration factor of 60 for Pb(II). The method can be used as screening to estimate the total concentration of Pb(II) present in a large number of samples and thus avoiding the continuous use of expensive instrumentation in routine analysis. The results of determination have been found to be accurate and reproducible.

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