

Application of Modified Nanoclay Sorbent for Separation and Preconcentration Trace Amount of Cobalt

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(Received: 28 Nov. 2010 and Accepted: 13 Feb. 2011)

Abstract:

The present article reports on the application of modified organo nanoclay as a green, easily prepared and stable solid sorbent for the preconcentration of trace cobalt ion in aqueous solution. The organo nanoclay was modified by adsorption of 5-(4-dimethyl amino-benzylidene) rhodanin reagent onto it. The sorption of Co^{2+} ions was quantitative in the pH range of 7.0 to 8.5, whereas quantitative desorption occurs instantaneously in 5.0 mL of $2.0 \text{ mol L}^{-1} \text{ HNO}_3$. The eluted solution was aspirated directly into the flame of atomic absorption spectrometry (FAAS). Linear range for determination of cobalt was maintained between 0.176 ng mL^{-1} to $15.0 \text{ } \mu\text{g mL}^{-1}$ in initial solution. Relative standard deviation for ten replicated determination of $1.0 \text{ } \mu\text{g mL}^{-1}$ of cobalt was $\pm 2.34\%$. Detection limit was 0.1 ng mL^{-1} in initial solution ($3S_{b,p}$, $n=10$) and preconcentration factor was 170. The sorption capacity of modified nanoclay for Co (II) was evaluated 0.56 mg per g of sorbent. The effects of the experimental parameters, including the sample pH, flow rates of sample and eluent solution, eluent type, breakthrough volume and interference ions were studied for preconcentration of Co^{2+} . The proposed method was applied for determination of cobalt in water samples.

Keywords: Nanoclay application; Cobalt determination; Preconcentration

1. INTRODUCTION

Due to industrial facilities, heavy metal contents in environmental samples have increased. So, it is necessary to develop reliable, fast, and sensitive methods for the determination of heavy metals in environmental and biological samples. Trace elements, such as cobalt, are of great interest because of many hazardous effects on human beings [1]. On the other hand, the direct determination of trace metals in environmental waters by FAAS is very difficult owing to low levels of metal ions. One way to solve this problem is the separation and preconcentration of the ion of interest in order to enhance the detection limit, selectivity and, thereby, to improve the precision and accuracy of

analytical results. Solid-phase extraction (SPE) is one of the several techniques used for these purposes [2]. In SPE various sorbents have been used, such as thiol cotton [3], activated carbon [4], silica gel [5], adsorption resin [6], microcrystalline naphthalene [7], Amberlite XAD resin [8, 9], synthetic zeolite [10], natural analcime zeolite [11], natural natrolite zeolite [12], modified kaolinite [13] and carbon nanotubes [14]. Properties of SPE sorbents are as follows: porous and large surface area, reversible adsorption, purity and low leach ability, good chemical stability, good surface contact with sample solution, and high percentage recovery [15].

In recent years, great attention has been paid to the application of nano structure materials. Because clay and

Table 1: Obtained recoveries in choosing the eluent type

Eluent (5.0 mL)	Concentration (mol L ⁻¹)	Recovery (%)
HNO ₃	2.0	98.0
H ₂ SO ₄	2.0	80.3
HCl	2.0	84.9
S ₂ O ₃ ²⁻	0.5	75.4

Conditions: Co, 5.0 µg; sample flow rate, 2 mL min⁻¹; Instrumental settings: Wavelength, 240.7 nm; lamp current, 7.0 mA; slit width, 0.2 nm; acetylene flow, 1.0 L min⁻¹; air flow (as oxidant), 3.5 L min⁻¹.

Table 2: Effect of interferences

Interference	Tolerance limit (mg)	Recovery (%)
Ca ²⁺	1200	98.8
Mg ²⁺	800	98.2
Fe ³⁺	200	98.4
Mn ²⁺	60	97.8
Cd ²⁺	120	98.6
Zn ²⁺	100	97.4
Pb ²⁺	200	98.3
Cu ²⁺	50	97.6
Ni ²⁺	40	97.4
Al ³⁺	1500	97.3
HPO ₄ ²⁻	700	97.5
PO ₄ ³⁻	600	97.5
H ₂ PO ₄ ⁻	750	97.3
EDTA	0.1	96.8

Conditions: Co, 5.0 µg; sample flow rate, 2 mL min⁻¹; eluent solution, 5.0 mL HNO₃ with a flow rate 1 mL min⁻¹; Instrumental settings: Wavelength, 240.7 nm; lamp current, 7.0 mA; slit width, 0.2 nm; acetylene flow, 1.0 L min⁻¹; air flow (as oxidant), 3.5 L min⁻¹.

clay minerals have primary particles with at least one dimension in the nanometer scale, they may be regarded as nanomaterials of geological and pedological origin [16]. Normally, organic surfactants are used to make the surface of clay platelets organophilic and swell the clay galleries. An organophilic surface and interlayer environment can be produced by replacing naturally occurring inorganic exchangeable cations with a variety of organic cations, such as long chain alkyl ammonium ions [17]. These modified organoclays are used in a wide range of applications, including the adsorbents for organic pollutants [18] and metal ions [19]. Because of their small particle size, the specific surface area of clays (both external and internal) and clay minerals extends to a few hundred m²/g. The nano-size dimension, extensive surface area, and peculiar charge characteristics of nanoclay materials lie behind their large propensity for taking up ions and organic compounds [20]. Therefore, the nanoclay may be suitable for preconcentration in solid phase extraction.

The aim of the described research is to develop application of modified nanoclay as a new sorbent for separation and preconcentration of trace amounts of Co²⁺ ions and to develop a simple, sensitive, rapid, and economical method for AAS determination of trace amount of Co²⁺ ion after separation and preconcentration onto nanoclay which was already loaded with 5-(4-dimethyl amino-benzylidene) rhodanin.

2. EXPERIMENTAL

2.1. Apparatus

A Varian model SpectrAA 220 atomic absorption spectrometer was used for measuring Co²⁺ in an air-acetylene flame. The operating conditions were as follows: wavelength, 240.7 nm; lamp current, 7.0 mA and slit width, 0.2 nm. The acetylene flow and the air flow were 1 and 3.5 L min⁻¹, respectively. The pH measurement was carried out using a Metrohm pH meter (model 827) with a combined pH glass electrode calibrated against two standard buffer solutions at pH 4.0 and 7.0. A funnel-tipped glass tube (80×10 mm) was used as a column for preconcentration. All glassware and columns were washed with a mixture of concentrated hydrochloric acid and concentrated nitric acid (1:1) before application.

2.2. Reagents and materials

High purity reagents from Sigma (St. Louis, MO, USA) and Merck (Darmstadt, Germany) were used for the preparation of all standard and sample solutions. Stock solutions were prepared daily from Co²⁺ standard solution (1000.0 mg L⁻¹, Merck) by serial dilution water. A 0.05% solution of 5-(4-dimethyl amino-benzylidene) rhodanin in ethanol was prepared. Buffer solutions were prepared from 0.5 mol L⁻¹ of acetic acid and 0.5 mol L⁻¹ of sodium acetate for pH range of 3 to 6, from 0.1 mol L⁻¹ of potassium dihydrogen phosphate and 0.1 mol L⁻¹ disodium hydrogen phosphate for pH 6-8 and from 0.5 mol L⁻¹ of ammonia and 0.5 mol L⁻¹ of ammonium acetate for pH 8-10. The nanoclay particles are organically modified montmorillonite in a platelet form, i.e. 10 µm long, 1 µm wide and 50 nm thick, and 600 m²g⁻¹ surface area with trade name of Nanomer I30E from Nanocor Company (USA).

2.3. Preparation of modified nanoclay

Industrial purified commercial modified nanoclay was washed with 2 mol L⁻¹ of HCl, and then, was dispersed in the 0.05% solution of 5-(4-dimethyl amino-benzylidene) rhodanin in ethanol at room temperature, heated to 40°C, with vigorous stirring for 8 h for the adsorption of 5-(4-dimethyl amino-benzylidene) rhodanin onto nanoclay. The sample was filtered, washed, and was dried at 80°C and stored until use.

2.4. Preparation of column

500 mg of modified nanoclay was added into a funnel-tipped glass tube (80×10 mm) and used as a column for preconcentration. Before sample is loaded the column must be preconditioned by passing a buffer solution. The column could be used repeatedly for 10 times after washing with distilled water.

2.5. General procedure

Initially, distilled water and buffer solution were passed through the column for column conditioning, then an aliquot of cobalt solution (containing 0.15 to 75.0 µg) was placed in a 50 mL beaker and 4 mL of buffer solution with pH

Table 3: Analysis of cobalt ion in standard sample

Sample	Composition (%)	Found (%) [*]	Recovery (%)
NKK No. 916 Aluminum alloy	Si, 0.41; C, 0.41; Fe, 0.54; Mg, 0.10; Cr, 0.05; Sn, 0.05; Zn, 0.30; Ti, 0.10; Pb, 0.04; Sb, 0.01; B, 0.0006; Zr, 0.05; Co, 0.03; Mn, 0.11; Bi, 0.03; Ni, 0.06; V, 0.02; Cu, 0.27.	0.031±0.002	103.3

Conditions and instrumental setting were same as Table 2

^{*} Mean± standard deviation (n=4)

Table 4: Determination of cobalt in the water samples

Sample	Found (ng mL ⁻¹) [*]
River water (Shahdad, Kerman)	12.4±0.3
Well water (Kerman University)	3.84±0.07
Spring water (Sardooieh, Jiroft)	7.42±0.11
Mineral water	2.15±0.04

Conditions and instrumental setting were same as Table 2

^{*} Mean± standard deviation (n=4)

Table 5: Comparison of the present method with other methods for preconcentration and determination of cobalt

Technique	Sorbent	D.L. (ng mL ⁻¹)	Recovery (%)	Preconcentration factor	Ref.
Spectrophotometry	Naphtalene	30	96	30	22
Spectrophotometry	XAD-4	35	97	200	23
FAAS	C18-silica	3.2	98	17	24
FAAS	Nano Clay	0.1	97.1	170	Present work

of 7.5 was added to it. This solution was passed through the column at a flow rate of 2 mL min⁻¹. After passing this solution, the column was eluted with 5 mL of deionized water. Adsorbed Co²⁺ ions on the column were eluted with 5.0 mL of HNO₃

2 mol L⁻¹ at a flow rate of 1 mL min⁻¹. The eluted solution was aspirated directly into the flame of atomic absorption spectrometry and compared with a blank prepared in the same manner without the addition of Co²⁺.

3- RESULTS AND DISCUSSION

Preliminary experiments showed that although, nanoclay has a low tendency for retention and adsorption of Co^{2+} (less than 40%), it is not selective for separation of cobalt ions. Therefore, the nanoclay isn't considered as a suitable sorbent for separation of cobalt ions. A recent work [21] indicates that nanoclay can be absorbed by organic materials. So, we added 5-(4-dimethyl amino-benzylidene) rhodanin ligands to nanoclay and then the modified nanoclay was used as a sorbent for separation of Co^{2+} ion. The results were shown that the recovery of cobalt ions by using modified nanoclay is higher than 97%. Moreover, modified nanoclay is selective for separation of Co^{2+} ion. In order to obtain highly sensitive, accurate, and reproducible results, analytical parameters including pH, type and volume of eluent solution, breakthrough volume and flow rates of sample and eluent were optimized for preconcentration of Co^{2+} ion.

3.1. Effect of the sample pH

As pH is one of the most important analytical factors in the solid phase extraction of metal ions [15], the influences of aqueous solution pH on the recovery of cobalt ions on modified nanoclay were investigated. Adsorption studies were carried out at different pH, keeping the other variables constant. The sorption percent of cobalt ion on the sorbent surface as a function of the pH of the sample solution was evaluated. It was found that the sorption percent of Co(II) depends on the pH of the sample solution. The optimum pH range was around 7.0-8.5 and therefore, the pH was maintained at approximately 7.5 with hydrogen phosphate buffer in subsequent studies.

3.2. Sorption capacity

The sorption capacity of 5-(4-dimethyl amino-benzylidene) rhodanin loaded modified nanoclay was determined by passing $30 \mu\text{g mL}^{-1}$ Co (II) ions, followed by the determination of retained Co (II) ions using FAAS. The maximum capacity of the sorbent was 0.56 mg of Co^{2+} per gram of sorbent. The 5-(4-dimethyl amino-benzylidene) rhodanin loaded modified nanoclay sorbent was subjected to several loadings with the sample solution and

subsequent elution. It was found that the adsorption properties of the adsorbent remained constant after 10 cycles of sorption and desorption.

3.3. Effect of flow rate of sample

Flow rate of the sample solution is a measure of the contact time between the sample solution and the sorbent. The results showed that the flow rate variation in the range of $0.5\text{--}3.5 \text{ mL min}^{-1}$ did not have a significant effect on the sorption of the rhodium. So, it was concluded that the adsorption of Co^{2+} ion on modified nanoclay is relatively rapid. In order to achieve good precision, a flow rate of 2 mL min^{-1} was therefore chosen for further studies.

3.4. Selection of eluent

Desorption of the adsorbed material on the solid phases is an important step for the solid phase extraction studies. A series of solvents such as, HNO_3 , HCl , H_2SO_4 and $\text{S}_2\text{O}_3^{2-}$, were used in order to find the best eluent for desorption of Co^{2+} ion from the sorbent surface. The results are shown in Table 1. It can be seen that the best recovery was achieved when HNO_3 was used as eluent. It was also found that 5.0 mL of this solvent was sufficient to elute the complex from modified nanoclay.

3.5. Effect of eluent flow rate

The effect of eluent flow rate on desorption of Co^{2+} ion from the sorbent surface was studied in the range of $0.5\text{--}3.5 \text{ mL min}^{-1}$. Flow rate of 1 mL min^{-1} was chosen in subsequent work.

3.6. Breakthrough volume

When solutions containing $1.0 \mu\text{g}$ of cobalt in 250, 500, 750, 800, 850, 900, 950 and 1000 mL of water were passed through the columns, the Co (II) was quantitatively retained in all cases. So, it was concluded that the breakthrough volume of the method under optimum conditions should be greater than 850 mL. Consequently, by considering the final elution volume of 5.0 mL of HNO_3 , and a breakthrough volume of 850 mL, a preconcentration factor of 170 was easily achievable.

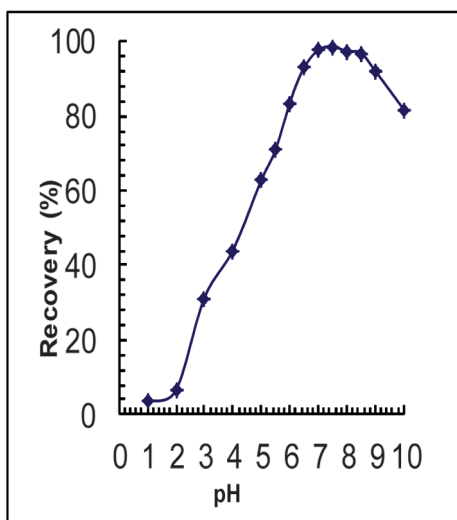


Figure 1: The effect of sample solution pH on the recovery of Co^{2+}

Conditions; Co, 5.0 μg ; sample flow rate, 2 mL min⁻¹; eluent solution, 5.0 mL HNO₃ with a flow rate 1 mL min⁻¹; Instrumental settings: Wavelength, 240.7 nm; lamp current, 7.0 mA; slit width, 0.2 nm; acetylene flow, 1.0 L min⁻¹; air flow (as oxidant), 3.5 L min⁻¹.

3.7. Interferences

The interferences of coexisting ions in binary mixtures of Co (II) with foreign ions were studied on the percent recovery of cobalt (1.0 $\mu\text{g mL}^{-1}$). After introducing the binary solution into a column, the adsorbed cobalt ion was eluted by HNO₃ solvent. The content of cobalt ions in effluents was determined using FAAS, and the recoveries were calculated. The results, summarized in Table 2, clearly indicate that most of the tested ions do not interfere with the determination of cobalt. The tolerance limit was set as the amount of foreign ions required to cause a $\pm 4\%$ error.

3.8. Analytical figure of merits

Analytical figures of merit were evaluated for the determination of cobalt according to the recommended procedure. Under optimum conditions, the calibration curve was linear from 0.176 ng mL⁻¹-15.0 $\mu\text{g mL}^{-1}$ in initial or 0.03 to 15.0 $\mu\text{g mL}^{-1}$ in final solution with a correlation coefficient (R^2) of 0.9997. The recommended procedure was repeated ten times to find the relative standard

deviation in the determination of 1.0 $\mu\text{g mL}^{-1}$ of Co (II) ion which RSD was found to be $\pm 2.34\%$. The obtained limit of detection 0.176 ng mL⁻¹ was based on three times the standard deviation of the blank solution measurements (n=10) in original solution.

3.9. Determination of cobalt in standard samples

The accuracy and applicability of the proposed method has been applied to the determination of cobalt in Nippon Keikinokogyo (NKK) CRM, No. 916. A 0.1 gram sample of the standard alloy was dissolved completely in 10 mL of hydrochloric acid 6 mol L⁻¹ by heating in a water-bath at 85°C. The solution was cooled, filtered and diluted to 100.0 mL with distilled water in a standard flask. An aliquot of this sample was taken in a 25 mL beaker and the general procedure was applied. The results obtained are shown in Table 3. These results are in agreement with certified values implying that the proposed method have good accuracy.

3.10. Analysis of water samples

In order to test the applicability and reliability of the proposed method, tap water, river water, spring, mineral water and well water samples were analyzed. For this purpose, 80.0 mL of each sample was preconcentrated in accordance with the proposed method. The results are shown in Table 4.

4. CONCLUSION

The present study demonstrates the use of modified nanoclay as a green sorbent in the preconcentration of cobalt ion in water samples. The preparation of modified nanoclay is simple and low cost. This sorbent is simple and has low cost which can be used several times without a marked loss in sorption capacity. The developed method is simple, rapid, precise and reliable offering a higher preconcentration factor and lower detection limit for Co²⁺ ion comparing with the other sorbents [22-24]. Table 5 compares the proposed method with those reported previously for the determination of cobalt after preconcentration procedure. It shows that the proposed method has a low detection limit compared with previous studies [22-24] and it allows the determination of ng mL⁻¹ levels of cobalt. The method is also economical due to the possibility of multiple uses of the sorbent.

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