ISSN : 0974-7419 Volume 11 Issue 6

Trade Science Inc.

Analytical CHEMISTRY

An Indian Journal

Full Paper

ACAIJ, 11(6) 2012 [245-248]

Preparation of morin modified nanoclay as a sorbent and its application to pre-concentration of iron from environmental water samples

Mostafa Khajeh

Department of Chemistry, University of Zabol, P. O. Box 98615-538, Zabol, (IRAN)

E-mail: m_khajeh@uoz.ac.ir

Received: 22nd February, 2012 ; Accepted: 22nd March, 2012

ABSTRACT

A new, simple and fast method that utilizes morin-modified nanoclay as a solid phase extraction has been developed for separation and pre-concentration of trace amount of iron (III) from environmental water samples prior to the measurement by flame atomic absorption spectrometry (FAAS). Some factors influencing the recovery of iron including pH, sample flow rate, amount of morin, type, flow rate and least amount of the eluent for elution of the iron from nanoclay were studied and optimized. Under the optimum conditions, the detection limit of this method was 0.12 μg L^{-1}, and the relative standard deviation (RSD%) was 2.8% (n = 10, c = 50 μg L^{-1}). The developed procedure was applied to the recovery and determination of iron in water samples.

KEYWORDS

Iron;
Nanoclay;
Solid phase extraction;
Water samples.

INTRODUCTION

Iron is the fourth most abundant element in the earth's crust. It is widely present in the tap, well, pond, underground and river water and this element is essential for the biological samples[1,2]. Iron and its compounds have widespread industrial application including constructional material for drinking water pipes, food colors, coagulants in water treatment, pigments in paints and plastics. Therefore, high quantities of this element are discharged into the environment.

Clay is natural, fine grained, earthy materials composed largely of a group of crystalline minerals. Clays have been employed for some year and still keep their position among the very important industrial materials[3,4]. They have been also used for difference purposes in chemical studies such as adsorption of difference inorganic and organic materials[3,5]. One of the most important of usage of clay is separation and preconcentration of element. Krikorian and Martin have been investigated solid phase extraction conditions for copper(II), cadmium(II), silver(I), nickel(II) and lead(II) ions on modified clays[6]. Adsorption conditions for uranium on Turgutlu and Kula clays have been investigated by Akcay and Kurtulmus[7].

The traditional separation/pre-concentration procedures for element including liquid-liquid extraction, coprecepitation, ion exchange and etc. these procedures often need large amount of organic solvents, which are harmful to health and cause environmental problems. Nowadays, solid phase extraction procedure is one of the most effective pre-concentration procedures due to of its advantages such as simple, high enrichment factor and flexibility to select the solid phase for

Full Paper

optimum results[8]. Therefore, the solid phase extraction was widely used for the pre-concentration of target analytes and the removal of matrix interferences (clean up) in various samples.

The purpose of this work was to develop a simple, fast and sensitive method for pre-concentration and determination of iron in water samples using nanoclay modified with morin. The adsorption and elution conditions for preconcentration and determination by FAAS have been optimized. Finally, the developed procedure was verified by determination of iron in water samples.

EXPERIMENTAL

Apparatus

A Konik Won M300 (Barcelona, Spain) flame atomic absorption spectrometer (FAAS), equipped with hollow cathode lam and acetylene-air burner was used for the determination of iron. The wavelengths and bandwidth were set to 248.3 nm and 0.2 nm, respectively. The pH was determined with a model 630 Metrohm pH meter with combined glass-calomel electrode.

Materials

3,5,7,2',4'-pentahydroxyflavone (morin) was obtained from Merck (Darmstadt, Germany). All acids used were of the highest purity available from Merck. A stock solution of Iron (III) (1000 mgL^{-1}) was prepared by dissolving the proper amount of $FeCl_3.6H_2O$ in double distilled water. Dilute solutions were prepared by an appropriate dilution of the stock solution in double distilled water.

Extraction procedure

The road dust samples were collected from different roadsides in Sistan & Balouchestan province, Iran. The samples washed with de-ionized water several times to remove any dust and other water-soluble impurities. The washed clay was dried at 105 °C for 5 h, ground, passed through a sieve of 200 meshes. A total of 2.0 g of nanocaly was poured into the SPE column. A polyethylene frit was placed at both ends to prevent loss of the nanoclay during the sample loading. The column was treated with 5 mL methanol and then with 5 mL of 0.5 mol L^{-1} nitric acid. Finally, the column was washed with de-ionized water until free from acid. For modified of nanoclay, a solution of 50 mg morin in 2 mL ethanol was poured into the column allowed to penetrate inside the sorbent completely. A portion of aqueous sample solution containing iron (III) ions was prepared, and then it was adjusted to the desired pH value. After that, this solution was passed through the column. The complexing between iron and morin was occurred on the nanoclay and the retention of iron was occurred on this sorbent. Finally, the Fe(III) ions retained with the nanoclay was eluted using nitric acid as elution solvent. The eluent was analyzed for the determination of iron concentration with FAAS.

RESULTS AND DISCUSSION

Effect of pH

In the SPE procedures for metal ion pre-concentration based on chelation, the pH of the sample solution is one of the main effective parameter for quantitative extraction of the target analytes. Because this important point, the effects of pH were studied at the pH range 2.1-5.5. The results was shown in Figure 1, the quantitative extraction (> 97%) was obtained in the pH 5.1. This results showed the complex of Fe(III)-morin could be decomposed at high acidity. Therefore, the subsequent studied was performed with pH 5.1.

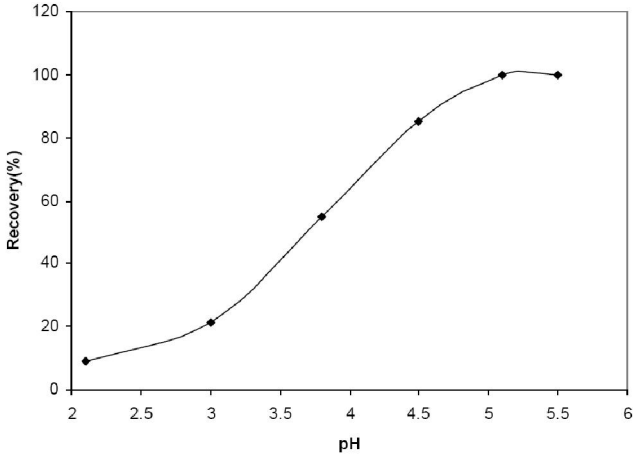

Figure 1 : Effect of pH on the recovery of iron ions.

Effect of the amount morin

The effect of the ligand amount in the pre-concentration of iron ions was checked. The results showed that the recovery was increased from 0.0 to 50.0 mg of morin. Hence, the next studied was performed with 50.0 mg of morin.

Effect of sample solution and eluent flow rates

The sample solution and eluent flow rates are very important parameters because the retention of iron ions on the nanoclay adsorbent depends upon them. In this study, different flow rates, 1.0 to 10.0 mL min^{-1} for sample solution and 1.0 to 5.0 mL min^{-1} for eluent were investigated (Figure 2). The results showed that the flow rate has a strong effect on the extraction of Fe(III) ions. The extraction of Fe(III) ions was decreased with an increase in flow rates. The quantitative extraction (>97%) was obtained with 5.0 mL min^{-1} for sample solution and 3.0 mL min^{-1} for eluent flow rates. Therefore, a flow rate of 5.0 mL min^{-1} for sample solution and 3.0 mL min^{-1} for eluent were selected as optimum flow rates.

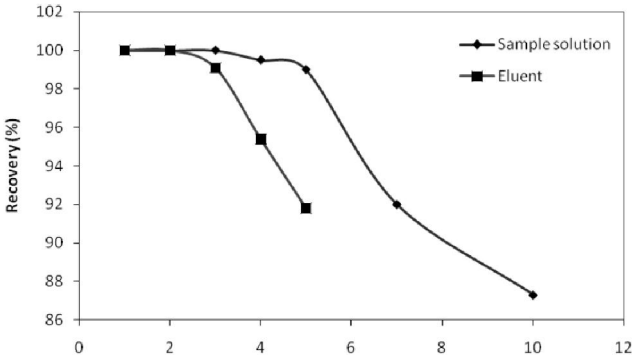

Figure 2 : Effect of flow rate on the recovery of iron ions

Effect of concentration and volume of elution solution

The elution of iron from the sorbent material was studied by using various concentrations (1-3 molL^{-1}) and volume (1-5 mL) of nitric acid. The results showed that the quantitative elution was obtained at concentrations higher than 1.5 mol L^{-1} and 3 mL volume of nitric acid. Therefore, 3.0 mL of 1.5 mol L^{-1} nitric acid was used as eluent in the next experiments.

Effect of sample volume

In order to obtain high pre-concentration factor, the influence of the sample volume on the extraction efficiency of Fe(III) ions on nanoclay was investigated in the range of 25-700 mL. The results showed that the recovery of Fe(III) ions was very efficient (>97%) in the sample volume range of 25-500 mL. After that the recovery of this analyte was decreased. In this work, the pre-concentration factor was 167 for 500 mL sample volume due to the elution volume of 3 mL.

Effect of coexisting ions

To investigate the selective separation and determination of iron ions from its binary mixtures with diverse metal ions, an aliquot of aqueous solution (50 mL) containing 0.5 mg L^{-1} iron and amounts of other cations was taken and the recommended method was followed (TABLE 1). The results show that the Fe(III) recovery was almost quantitative (>97%) in the presence of diverse ions. Since the chloride, nitrate and sulphate salts were employed in this study without any interference, their respective anions pose no possibility of interference.

TABLE 1 : Investigation of tolerance limit of interfering ions on proposed procedure

Foreign ion	[Interfering ion]/ [iron ions]
Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}	500
Cu^{2+}, Mn^{2+}, Ag^+, Zn^{2+}, Ni^{2+}, Pb^{2+}	10

Analytical figures of merit

To determine the limit of detection (LOD) of the proposed procedure, a 50 mL of blank solution (n=10) was passed through the column under the optimal experimental conditions. The LOD was investigated as the concentration corresponding to three times standard deviation of the blank signals ($C_{LOD} = 3\,(S_d)_{blank}$) and found to be 0.12 µg L^{-1}. The relative standard deviation (RSD%) of the ten replicate determination was <2.8%, that indicated this method has good precision for the analysis of trace iron in the sample solution.

Analysis of real samples

The procedure was used to preconcentration and determines the concentration of iron in water samples. Additionally, the recovery experiments of different amounts of iron were performed, and the results are shown in TABLE 2.

TABLE 2 : Determination of iron in water samples (*N* = 3)

Samples	Iron content (µg L^{-1})		Recovery (%)
	Added	Found (RSD%)	
Tap water	-	59.1± 1.1	-
	50.0	108.9 ± 0.9	99.6
River water	-	42.7± 1.4	-
	50.0	92.8 ± 1.5	100.2
Well water	-	37.5 ± 0.8	-
	50.0	87.1 ± 0.7	99.2

Full Paper

CONCLUSION

A fast, simple, precise and cheap procedure is proposed for pre-concentration and determination of iron in a variety of water samples. The morin modified nanoclay was successfully applied for the extraction of Fe(III) ions with satisfactory results. This sorbent can be used at least 100 times for the experiments. A low detection limit, up to 0.12 $\mu g\ L^{-1}$ is advantages of this analytical method. The procedure could be applied for the pre-concentration of analytes ions from other matrices. As shown in TABLE 3, the characteristic data of the present procedure are compared with those reported in the literature.

TABLE 3 : Comparison of the published methods with the proposed method in this work

Enrichment method	Detection limit (μgL^{-1})	Enrichment factor	RSD%	Reference
SPE	0.15	75	3.0	[9]
SPE	0.34	75	1.5	[10]
SPE	0.88	109	<3.4	[11]
Nanoclay	0.12	167	2.8	This Work

REFERENCES

[1] A.Asan, M.Andac, I.Isildak; Chemical Paper, **64**, 424-428 **(2010)**.
[2] S.Ohno, M.Tanaka, N.Teshima, T.Sakai; Anal.Sci., **20**, 171-175 **(2004)**.
[3] M.Tuzen, E.Melek, M.Soylak; J.Hazardous Materials B, **136**, 597-603 **(2006)**.
[4] M.Ozer, F.Arslan, G.Onal; Key.Eng.Mater., **264**, 1439-1442 **(2004)**.
[5] A.Kaya, H.Y.Fang; Can.Geotech.J., **42**, 632-640 **(2005)**.
[6] N.Krikorain, D.F.Martin; J.Environ.Sci.Health.A, **40**, 601-608 **(2005)**.
[7] H.Akcay, F.Kurtulmus; J.Radioanal.Nucl.Chem. Lett., **200**, 529-544 **(1995)**.
[8] Y.Cui, X.Chang, X.Zhu, H.Luo, Z.Hu, X.Zou, Q.He; Microchem.J., **87**, 20-26 **(2007)**.
[9] X.Zhu, X.Chang, Y.Cui, X.Zou, D.Yang, Z.Hu; Microchem.J., **86**, 189-194 **(2007)**.
[10] X.Chang, N.Jiang, H.Zheng, Q.He, Z.Hu, Y.Zhai, Y.Cui; Talanta, **71**, 38-43 **(2007)**.
[11] A.Goswami, A.K.Singh; Anal.Bioanal.Chem., **374**, 554-560 **(2002)**.