Application of Crosslinked Carboxymethyl Konjac Glucomannan in Speciation of Dissolved Fe(II) and Fe(III) in Water Samples

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ABSTRACT: A new solid-phase extraction technique has been developed for the speciation of trace dissolved Fe(II) and Fe(III) in environmental water samples with a microcolumn packed with crosslinked carboxymethyl konjac glucomannan (CCMKGM) prior to its determination by flame atomic absorption spectrometry (FAAS). Various influencing factors on the separation and preconcentration of Fe(II) and Fe(III), such as the acidity of the aqueous solution, sample flow rate and volume, and eluent concentration and volume, have been investigated systematically and optimized. Fe(III) could be quantitatively retained by CCMKGM in the pH range of 3.0–7.0, then the retained Fe(III) on the CCMKGM was eluted with 5.0 mol L^{-1} HCl after cleaning with 0.01 mol L^{-1} HCl to eliminate Fe(II) and determined by FAAS. Total Fe was determined after the oxidation of Fe(II) to Fe(III) by H_2O_2, and Fe(II) concentration was calculated by subtracting Fe(III) from total iron. The adsorption capacity of CCMKGM for Fe(III) was found to be as high as 162.3 mg g^{-1}. The detection limit (3σ) for Fe(III) was 1.5 μg L^{-1} and the RSD was 3.5% ($n = 11$, $c = 20$ μg L^{-1}) with an enrichment factor of 50. The proposed method has been applied to the speciation of iron in water samples with satisfactory results. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3961–3966, 2009

Key words: crosslinked carboxymethyl konjac glucomannan; iron; speciation; flame atomic absorption spectrometry

INTRODUCTION

Iron is essential to most life forms. Both iron(II) and iron(III) play a central role in the biosphere, serving as an active centre in a wide range of proteins such as oxidases, reductases, and dehydrases. Its reactivity also drives numerous chemical processes in natural waters, and it is a significant factor in the evaluation of water quality.[1,2] So a great number of speciation studies of iron have been carried out, combining with divers sensitive detection techniques, such as spectrophotometry,[3–6] atomic absorption spectrometry (AAS),[7–9] ion chromatography (IC),[10] capillary electrophoresis (CE),[11,12] flow-injection chemiluminescence (FI-CL),[13,14] inductively coupled plasma-atomic emission spectroscopy (ICP-AES),[15,16] and inductively coupled plasma-atomic mass spectrometry (ICP-MS).[17] However, most of them involve complexing reagents in the process of separation, which may cause potential transformation of speciation and contamination.

Flame atomic absorption spectrometry (FAAS) is widely used for the determination of iron in many laboratories due to its advantages over ICP-AES or ETAAS, such as simple, inexpensive equipment, and less subject to interferences. However, this method is beset with problems of lack of selectivity and sensitivity compared to widely accepted ICP-MS, and GFAAS. Hence, combining a preconcentration step prior to FAAS determination is often resorted to by analytical researchers. Various techniques have been used for separation and preconcentration of iron, such as solvent extraction,[18,19] solid-phase extraction,[3,8,9,16,17,20] and cloud point extraction,[21,22] etc. Among these techniques, solid-phase extraction based on selective or simultaneous retention of Fe(II) and Fe(III) on sorbent is widely used for the speciation of iron in water samples for its simple, fast, inexpensive, without the addition of chelating agents, and the ability of online or offline combination with different detection techniques. Several solid sorbents, such as modified resin,[3] modified microcrystalline naphthalene,[16] modified nanometer-sized alumina,[17] cellulose,[23] chitosan,[24] and natural polymers[25] have been used for separation and preconcentration of iron species.

Konjac glucomannan (KGM), a water-soluble heteropolysaccharide of tubers from the *Amorphophallus*

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konjac plant, consists of 1,4-linked β-D-mannose and β-D-glucose units in a molar ratio of 1.6 : 1 with a low degree of acetyl groups at the side chain C-6 position and having an average molecular weight of 0.67–1.9 million.[26] It could be used as a potential sorbent for solid-phase extraction of metals with small modification. Recently, Niu et al.[27] have synthesized the crosslinked carboxymethyl konjac glucomannan (CCMKGM), derived from KGM by reacting with monochloroacetic acid and epoxy chloropropane, showed high capacity to adsorption of Pb(II), Cd(II), and Cu(II), indicating it could be used as a good sorbent for solid-phase extraction of heavy metals. To the best of our knowledge, CCMKGM has never been selected as a sorbent to investigate its adsorption behaviors on dissolved Fe(II) and Fe(III).

In this work, the CCMKGM was used for the first time as the sorbent for the speciation of dissolved Fe(II) and Fe(III). A new method using CCMKGM microcolumn has been developed for the separation and preconcentration of iron prior to its determination by FAAS. Experimental parameters affecting the preconcentration of iron, such as pH of the sample, sample flow rate and volume, eluent and interfering ions, were studied and optimized, and the proposed method was applied to the speciation of iron in tap and lake water samples.

EXPERIMENTAL

Instrumentation

A TAS-986 atomic absorption spectrometer (Beijing Purkinje General Instrument, Beijing, China) equipped with deuterium lamp background correction was used. An iron hollow cathode lamp operating at 3.0 mA was used as the radiation source. The wavelength, slit width, and observation height were set at 248.3 nm, 0.4 nm, and 6 mm, respectively. A UV–vis spectrophotometer (Nicolet 300 evolution) was used for the determination of visible absorbance at 510 nm. The pH values were measured with a PHS-3C pH meter (Rex Instrument Factory, Shanghai, China). A constant pump (Mode DHL-A, Shanghai Huxi Analysis Instrument Factory, Shanghai, China) was used in separation/preconcentration process. A PTFE microcolumn (10 mm × 1.0 mm i.d.) packed with CCMKGM was used in the manifold for separation and preconcentration. A minimum length of PTFE tubing with an i.d. of 1.0 mm was used for all connection.

Materials and reagents

Konjac glucomannan was purchased from Shiyan Huaxianzi Konjac Productions, China. The stock solution (1.0 g L^{-1}) of Fe(II) and Fe(III) was prepared by dissolving analytical grade of $Fe(NH_4)_2(SO_4)\cdot 6H_2O$ and $FeCl_3$ in 2% (v/v) HCl, respectively. Working standard solution was prepared fresh daily by stepwise dilution of the stock solution with Mill-Q water (Millipore, Japan). HCl was of the highest purity available. All other chemicals were of analytical grade and used without further purification. All containers used in this study were soaked in 10% HNO_3 for at least 24 h before rinsing thoroughly with Mill-Q water.

Synthesis of crosslinked carboxymethyl konjac glucomannan

CCMKGM was synthesized following the method reported by Niu et al.[27] with some modifications. Briefly, 7.5 g of konjac glucomannan dispersing in 50 mL of isopropyl alcohol was transferred to a 250 mL flask, then 7.5 mL of sodium hydroxide solution (50 wt %) was added dropwisely over 30 min while stirring at 50°C. At 0.5 h of reaction, 8.0 mL of 80 wt % monochloroacetic acid was added gradually. Mechanical stirring was continued for 3 h at 50°C. At this point, the mixture was adjusted to pH > 12 with 5.0 mol L^{-1} NaOH and crosslinking agent, epichlorohydrin, was added and crosslinking reaction was kept for another 2 h at 40°C. The mixture was then allowed to cool, neutralized with hydrochloric acid, washed with 95 wt % alcohol to remove impurities and then washed thoroughly with Milli-Q water, filtered, and pan-milled. The resulting powder was dried in vacuum for future use.

Column preparation

A total of 10 mg of CCMKGM was filled into a PTFE microcolumn (10 mm × 1.0 mm i.d.) plugged with a small portion of glass wool at both ends. Before use, 5.0 mol L^{-1} HCl and Milli-Q water were passed through the column in sequence for cleaning it. Then, the column was conditioned to the desired pH with 0.1 mol L^{-1} NH_4Cl buffer.

Procedure

A portion of aqueous sample solution containing Fe(II) and Fe(III) was prepared, and the pH value was adjusted to the desired pH with 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} $NH_3\cdot H_2O$. The solution was passed through the column by using a constant pump adjusted to the desired flow rate. After cleaning with 0.01 mol L^{-1} HCl to eliminate Fe(II), retained Fe(III) on the CCMKGM was eluted with 5.0 mol L^{-1} HCl and determined by FAAS. Total Fe was determined after the oxidation of Fe(II) to Fe(III) by H_2O_2, and Fe(II) concentration could be calculated by subtracting Fe(III) from the total iron. The

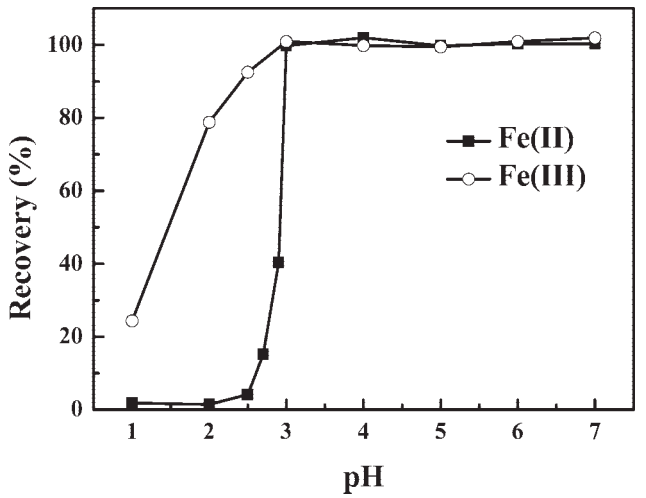

Figure 1 Effect of pH on the recoveries of Fe(II) and Fe(III). Concentration: 1.0 mg L^{-1}; sample volume: 10 mL; eluent: 2.0 mL of 0.01 mol L^{-1} HCl for Fe(II) and 2.0 mL of 5.0 mol L^{-1} HCl for Fe(III); sample flow rate: 1.5 mL min^{-1} for Fe(II) and 3.0 mL min^{-1} for Fe(III).

microcolumn could be used repeatedly after regeneration with 5.0 mol L^{-1} HCl solution and Milli-Q water, respectively.

Sample preparation

Lake water sample (pH 6.8) was collected from South Lake (Wuhan, China), and local tap water sample (pH 6.9) was freshly collected from the laboratory, after allowing the water to flow for 5 min. All water samples were filtered through a 0.45-μm membrane filter for analysis without further pH adjustment.

Water sample was divided into two parts: (i) Fe(III) determination: water sample (100 mL) was determined directly under the proposed procedure after filtered through a 0.45-μm membrane filter. (ii) Total iron determination: according to the procedure, 50 μL of 30% (W/V) H_2O_2 was added to 100 mL of water sample before column adsorption.

RESULTS AND DISCUSSION

Effect of pH

In the preconcentration studies, the pH value plays an important role in adsorption and separation of different ions on adsorption materials.[17] Therefore, the effect of pH on the retention of Fe(II) and Fe(III) on CCMKGM was studied in the range of 1.0–7.0, as depicted in Figure 1. Quantitative recoveries (>90%) were reached for both Fe(II) and Fe(III) at pH range of 3.0–7.0, which is a wide pH range compared with that of other analytical methods.[3,9,17] Thus, no buffer is required to control the pH values precisely in real water determination and a pH of 6.0 was selected in the study below.

Elution of Fe(II) and Fe(III)

It is found from Figure 1 that the recovery of Fe(II) at pH < 2 was negligible. For this reason, various concentrations of HCl were studied for the desorption of retained Fe(II) and Fe(III) on the microcolumn. Figure 2 shows the effect of HCl concentration on the recoveries of the retained Fe(II) and Fe(III). As can be seen, quantitative recovery (>90%) was found for Fe(II) with HCl concentration 0.01–5.0 mol L^{-1}, whereas the recovery of Fe(III) was rather low (<5%) as the concentration of HCl lower than 0.05 mol L^{-1} and did not reach 90% until HCl concentration higher than 4.0 mol L^{-1}. Accordingly, 0.01 mol L^{-1} HCl could be chosen as the suitable eluent to remove Fe(II) out of the microcolumn without loss of Fe(III). The effect of elution volume on the recovery of Fe(II) and Fe(III) was also studied by keeping the HCl concentration equal to 0.01 mol L^{-1} for Fe(II) and 5.0 mol L^{-1} for Fe(III), respectively. It was found that quantitative recoveries (>90%) for both Fe(II) and Fe(III) could be obtained with 2.0 mL HCl solution.

On the basis of the results above, it seems that quantitative separation of Fe(II) and Fe(III) retained on microcolumn could be performed by delicately choosing the eluent concentration of HCl. However, it was found that Fe(II) could not be determined directly in real water due to the serious interference on its adsorption on the microcolumn caused by coexistence ions as further experiments indicated. Therefore, Fe(III) was determined first under the proposed procedure, total iron was determined after the oxidation of Fe(II) to Fe(III),[4] and Fe(II) concentration could be calculated by subtracting Fe(III) from total iron.

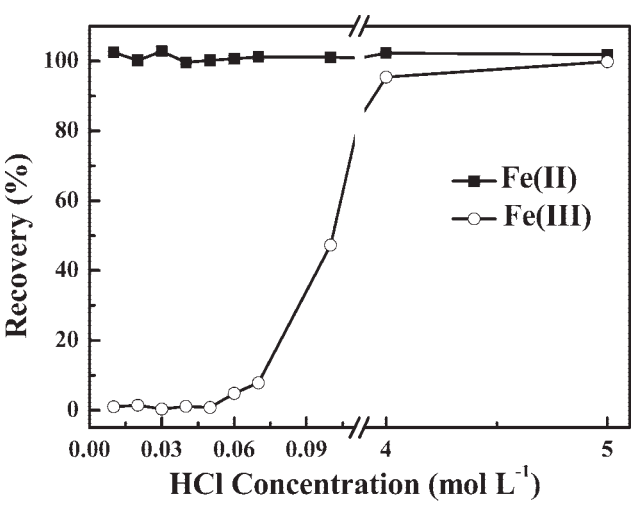

Figure 2 Effect of HCl concentration in the elution on the recovery of Fe(II) and Fe(III). Concentration: 1.0 mg L^{-1}; sample volume: 2.0 mL; elution volume: 5.0 mL; sample flow rate: 1.5 mL min^{-1} for Fe(II) and 3.0 mL min^{-1} for Fe(III); pH: 6.0.

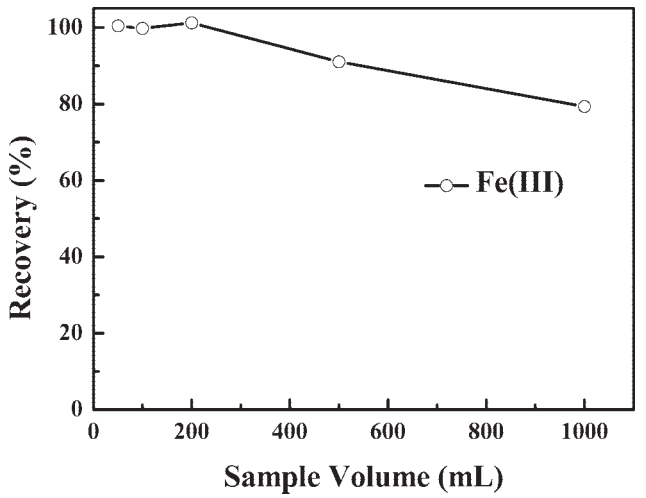

Figure 3 Effect of sample volume. Fe(III): 10 μg; pH: 6.0; eluent: 2.0 mL of 5.0 mol L^{-1} HCl; sample flow rate: 3.0 mL min^{-1}.

Effect of sample flow rate

The sample flow rate should be optimized to ensure quantitative adsorption along with minimum time required for sample processing. Therefore, the effect of this flow rate was examined under the optimum conditions (pH, eluent, etc.). It was found that the flow rate changing from 0.5 to 3.0 mL min^{-1} had no significant effect on the recovery of Fe(III). Thus, a flow rate of 3.0 mL min^{-1} is used.

Effect of sample volume

The influence of the sample volume on recovery of Fe(III) was also examined. For this purpose, sample solutions of 50, 100, 200, 500, and 1000 mL containing 10 μg of Fe(III) were passed through the column, and then treated according to the recommended procedure. As shown in Figure 3, the recovery of Fe(III) was quantitative (>90%) up to a sample volume of 500 mL.

In this work, for saving the time of analysis, a sample solution volume of 100 mL was adopted for the preconcentration of Fe(III) from water sample. Because the adsorbed Fe(III) can be eluted with 2.0 mL of 5.0 mol L^{-1} HCl, an enrichment of 50 was achieved by this procedure.

Adsorption capacity

The adsorption capacity is an important factor showing how much sorbent would be required to achieve quantitative recovery of the analytes in a given solution. The experiment was performed by taking 20 mg of CCMKGM into different 50 mL of buffer solutions (pH 3.0) with different Fe(III) concentrations. Those mixtures were shaken for 60 min at room temperature (25 ± 1°C) and then filtered. The filtrates were determined by FAAS. As a result, the adsorption capacity of CCMKGM for Fe(III) was calculated to be 162.3 mg g^{-1}.

As shown in Table I, CMKGM possess a higher adsorption capacity than the reported values of some similar solid sorbents for the same purpose, such as 90.09 mg g^{-1} for Fe(III) in chitosan[24] and only 11.3 mg g^{-1} for Fe(III) in modified resin,[3] which means less sorbent is needed in our method. This phenomenon could be related to a large number of the ionization of the carboxymethyl groups in CCMKGM, which could form complex with the Fe(III). In comparison with some of the reported SPE materials in the literature, another advantage of CMKGM is a feasible range of pH (3.0–7.0) could be chosen for preconcentration. That is to say, direct preconcentration of iron in the most of the environmental water samples could be conducted without precisely adjusting the pH values.

TABLE I
Characteristic Performance of Some Reported SPE of Fe(II) and Fe(III)

SPE material	Technique	pH[a]		Capacity (mg g^{-1})		Reference
		Fe(II)	Fe(III)	Fe(II)	Fe(III)	
Modified resin	GFAAS	–	3.2	–	11.3	3
Modified silica gel	FAAS	3.5–4.5	–	0.2	–	8
Modified resin	FAAS	–	8.0	–	–	9
Modified microcrystalline naphthalene	ICP-OES	>6.0	2.0–4.0	65.3	45	16
Modified nanometer-sized alumina	ICP-MS	–	5.5–6.5	–	5.5	17
Cellulose	FAAS	–	8.0	–	–	23
Chitosan	FAAS	5.0	5.0	64.10	90.09	24
CCMKGM	FAAS	3.0–7.0	3.0–7.0	–	162.3	This work

[a] Applicable pH range.

TABLE II
Tolerance Limits of Coexisting Ions

Coexisting	Tolerance limit of ions (mg L^{-1})
Na^+, K^+	3000
Mg^{2+}	2000
Ca^{2+}	1000
Cr^{3+}	700
Mn^{2+}	500
Zn^{2+}	400
Ni^{2+}	300
Cu^{2+}, Pb^{2+}, Al^{3+}	100
Cl^-, NO_3^-	3000
CO_3^{2-}	1500
CH_3COO^-, SO_4^{2-}	1000
PO_4^{3-}	200

pH: 6.0, eluent: 2.0 mL of 5.0 mol L^{-1} hydrochloric acid, flow rate of sample: 3.0 mL min^{-1}, concentration of Fe(III): 1.0 mg L^{-1}, sample volume: 10 mL.

Column reuse

The stability and potential regeneration of the column were investigated. The column can be reused after regenerated with 2.0 mL 5.0 mol L^{-1} HCl and 10 mL Mill-Q water, respectively and was stable up to at least 300 adsorption-elution cycles without decreasing in the recoveries of Fe(III). In fact, the same microcolumn was used throughout this work without replacing the SPE material.

Effect of coexistence ions

The effect of common coexisting ions was investigated. In these experiments, solutions containing 1.0 mg L^{-1} of Fe(III) and the added interfering ions were treated according to the recommended procedure. The tolerance limits of the coexisting ions, defined as the largest amount causing a change in the recovery of Fe(III) less than 10%. It can be seen that the presence of coexisting ions has no influence on the determination of Fe(III) under the selected conditions (Table II).

TABLE III
Analytical Results for Fe(II) and Fe(III) in Synthetic Water Samples[a]

Contains (μg L^{-1})		Found (μg L^{-1})		Recovery (%)	
Fe(II)	Fe(III)	Fe(II)[b]	Fe(III)	Fe(II)	Fe(III)
50	50	47.42 ± 1.07	49.58 ± 0.95	94	99
0	50	ND[c]	50.42 ± 0.76	–	101
50	0	46.08 ± 0.87	ND[c]	92	–

[a] Mean ± standard deviation ($n = 3$).
[b] Calculated value.
[c] Not detected.

Analytical performance

The calibration curve for iron was linear in the concentration range from 0.5 to 10 mg L^{-1} with a correlation coefficient of 0.9976 under the optimum experimental conditions. The detection limit of this method, evaluated as the concentration corresponding to three times the standard deviation of 11 replicate measurements of blank solution using the preconcentration method, was found to be 1.5 μg L^{-1} for iron. The precision of this method (RSD),

TABLE IV
Determination of Fe(II) and Fe(III) in Natural Water Samples[a]

	Added (μg L^{-1})		Found (μg L^{-1})			Recovery (%)	
Samples	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Total	Fe(II)	Fe(III)
Proposed method							
GSB	0	0	ND[b]	271.7 ± 10.9	273.7 ± 16.0	–	–
07-1188-2000[d]	100	100	104.7 ± 7.4[c]	370.4 ± 8.2	475.2 ± 15.6	105	99
Tap water	0	0	ND[b]	29.63 ± 1.63	31.59 ± 0.87	–	–
	50	50	45.12 ± 1.48[c]	78.17 ± 1.69	123.28 ± 1.54	90	92
Lake water	0	0	ND[b]	34.81 ± 1.78	33.92 ± 1.60	–	–
	50	50	47.80 ± 1.37[c]	84.43 ± 3.67	132.23 ± 2.63	96	98
1,10 phenanthroline							
GSB	0	0	ND[b]	289.3 ± 12.5	–	–	–
07-1188-2000[d]	100	100	93.00 ± 0.0	389.3 ± 20.5	–	93	100
Tap water	0	0	ND[b]	28.00 ± 5.00	–	–	–
	100	100	92.67 ± 4.71	132.67 ± 9.43	–	93	105
Lake water	0	0	ND[b]	36.33 ± 6.23	–	–	–
	100	100	99.33 ± 4.71	136.00 ± 8.16	–	99	99

[a] Mean ± standard deviation ($n = 3$).
[b] Not detected.
[c] Calculated value.
[d] The Environmental Water Reference Material (China): the certified value of Fe concentration is 287 ± 25 μg L^{-1}.

examined by 11 replicate measurements of 20 μg L^{-1} of Fe(III), was found to be 3.5%.

Analytical applications

Synthetic aqueous mixture of Fe(II) and Fe(III) was analyzed to check the accuracy and precision of the proposed method. As given in Table III, the concentration of Fe(II) and Fe(III) obtained with our method is in good agreement with the expected values.

The accuracy of the proposed method was further demonstrated by analyzing the Environmental Water Reference Material GSB 07-1188-2000 (No. 202415). The results were given in Table IV. The *t* test at 95% confidence was done, the value of *t* is 1.15, less than the critical value of $t_{0.05,2}$ that is 4.30, showing that there exist no distinctive difference between the determined value and certified value. However, no Fe(II) was found in GSB 07-1188-2000 (No. 202415). This can be attributed to the reason that the reference sample was dissolved in the HNO_3 and the Fe(II) ions were oxidized.[17]

The proposed method was applied to the determination of dissolved Fe(II) and Fe(III) in tap water and lake water. The recovery experiments of different amounts of iron were also carried out along with the determination, and the results are shown in Table IV. The results indicated that the recoveries were reasonable for trace analysis, in a range of 90–98%. The Fe(II) and Fe(III) speciation results obtained from the water samples were compared with those results obtained using the 1,10-phenanthroline spectrophotometric method.[28] The results were found to be in good agreement.

CONCLUSIONS

The adsorption behaviors of Fe(II) and Fe(III) on CCMKGM were studied systemically, and a simple, sensitive, and reliable method for the separation and determination of iron species in natural water using CCMKGM-packed microcolumn coupled with FAAS was developed. Compared with most of the analytical methods for the speciation of iron, the advantages of the proposed procedure can be summarized as follows: (1) a wide range of pH 3.0–7.0 could be applied to the preconcentration of Fe(III) in aqueous phase, meaning no need of precise control of the pH values with buffer for the analysis of natural water samples; (2) no chelating agent was added in the process of separation, avoiding the risk of potential transformation of speciation and contamination; (3) the adsorption capacity of CCMKGM is much higher than other similar solid sorbent for Fe(III); (4) the CCMKGM is quite durable and can be used repeatedly at least 300 cycles with simple regenerating treatments. Furthermore, this procedure could be combined with other methods of analysis, such as ICP-AES and ICP-MS, and used as an online preconcentration system.

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