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ORIGINAL PAPER

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Improved immobilization of 8-hydroxyquinoline on polyacrylonitrile fiber and application of the material to the determination of trace metals in seawater by inductively coupled plasma mass spectrometry

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Abstract A modified synthetic method has been developed for immobilization of 8-hydroxyquinoline on polyacrylonitrile fiber. The synthetic conditions, e.g. reagent concentration, reaction temperature and time, were optimized. The features of the newly-modified fiber are higher exchange capacity compared with most other materials containing immobilized 8-hydroxyquinoline, better mechanic characteristics, high stability at both high and low pH, and ease of synthesis. This modified fiber can concentrate and separate trace metals from matrices with higher concentrations of alkali and alkaline earth elements. To validate the characteristics of the modified fiber, trace metals Ag, Be, Cd, Co, Cu, Mn, Ni, Pb, and Zn in the certified reference materials river water (SLRS-4) and seawater (CASS-4, NASS-5, SLEW-3) were preconcentrated before determination by inductively coupled plasma mass spectrometry. Good agreement was obtained between the data obtained by this method and the certified values.

Keywords 8-Hydroxyquinoline immobilized polyacrylonitrile fiber · Trace metals · Sea water · Inductively coupled plasma mass spectrometry

Introduction

Inductively coupled plasma mass spectrometry (ICP–MS) is one of the most accurate, sensitive, and reliable techniques for the determination of trace metals and has been widely used for determination of trace elements in environmental samples. Its low tolerance of dissolved solids (<0.1%, w/v), however, prohibits the direct analysis of trace elements in seawater by ICP–MS, because of the problem of salt deposition on the torch, sampling interface, or ion lenses. In ICP–MS interferences fall broadly into two groups, "spectroscopic", and "non-spectroscopic" or "matrix effects". The extent of the interferences depends on many factors including extraction geometry, plasma and nebulizer system operating conditions, and, most importantly, on the nature of the analytes and matrix. To minimize interferences many approaches have been recommended, including instrument optimization, use of mixed gases and/or "dry" sample introduction, sample dilution, sample-matrix matching, and use of internal standards, etc. [1]. It should be pointed out that these interferences are usually related to the nature of the sample matrix and much can be done to minimize or even eliminate potential problems by careful sample preparation. It must be admitted that for simultaneous multi-element determination by ICP–MS in a complex matrix such as seawater separation and/or pre-concentration methods are the first choice [1, 2, 3].

8-Hydroxyquinoline is a well-characterized chelating organic ligand. It can form covalent compounds with over 60 metal ions under controlled pH conditions, and its preference for transition and heavy metals to alkali and alkaline-earth elements is well known [4]. Trace elements are usually chelated with solution of 8-hydroxyquinoline and then extracted with organic solvent [5]. In comparison with the most commonly used solvent extraction enrichment procedures, however, column solid-phase extraction enables preconcentration of trace elements from larger volumes of sample, and so higher concentration factors, simple storage and easy transport of the pretreated samples can be achieved [6, 7, 8].

Much research has recently been performed to establish the most effective means of immobilization of 8-hydroxyquinoline on a number of suitable substances, including glass beads [9], silica gel [10, 11], polystyrene–divinylbenzene [12], and vinyl polymer agglomerate [13], and the characteristics of the different products have been compared [14]. 8-Hydroxyquinoline immobilized on silica gel is one of the most frequently used ion exchangers and is commercially available [14, 15, 16]. It is, however,

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unstable at high pH, leading to cleavage of the immobilized 8-hydroxyquinoline and potential trace metal contamination from the newly exposed silica surface [17, 18].

Fibers such as polyethylene, polypropylene, cellulose, and polyacrylonitrile, are good supports. They have high specific surface areas, approximately two orders of magnitude larger than that of a gel-structure granular ion-exchanger or 5–6 times that of a porous copolymer. The particle diameter of a fibrous ion exchanger is 1–2 orders of magnitude less than the mean diameter of a granular material. Fibers also differ from crosslinked granular polymers in the presence of linear or branched macromolecules, which might have swelling capacity [18]. Thus fibrous ion-exchangers have good kinetic and mechanical characteristics.

In our previous work, poly(acrylaminophosphonic dithiocarbamate) chelating fiber was developed and used to preconcentrate trace elements from seawater [2, 19]. The synthesis was, however, time-consuming – approximately four days. 8-Hydroxyquinoline has also been immobilized onto a polyacrylonitrile hollow fiber membrane [20, 21]. Because of the low mechanical strength of the membrane, however, it is easily damaged during the synthesis and the reaction conditions, e.g. reaction temperature and time, are limited leading to low yield and exchange capacity. These drawbacks also restrict its widespread application in analytical chemistry.

The aim of this study was to improve the synthetic route to immobilization of 8-hydroxyquinoline onto polyacrylonitrile fiber, to overcome the above-mentioned drawbacks of previous synthetic procedures. The conditions used in the newly recommended synthetic procedure, e.g. reagent concentration, reaction temperature and time etc., were optimized. The distinct features of the modified fiber include ease of synthesis, higher breakthrough capacity, better mechanical characteristics, and stability under highly acidic and alkaline conditions. The modified fiber has been applied to the preconcentration of trace elements in certified seawater and river water reference materials before determination by ICP–MS and good agreement was achieved between the data obtained by this method and the certified values.

Experimental

Reagents and solutions

Stock solutions of each trace metal for sample analysis, 1000 mg L^{-1}, were prepared by dissolving appropriate amount of metal oxide (Specpure, Johnson Matthey Chemicals) in nitric acid (67%, 5 mL). Single and multi-element standard solutions of concentration 10, 50, and 100 ng mL^{-1} were prepared from the stock solutions by serial dilution with dilute HNO_3. The final acid concentration of all standard solutions was fixed at 0.1 mol L^{-1} HNO_3.

All other reagents were of analytical grade or better. High purity water (18 MO cm) was used. Nitric acid was purified by sub-boiling distillation in a quartz still using ultrapure grade HNO_3 as feed. All other acids used were of ultrapure grade (Beijing Chemicals, China).

Polyacrylonitrile fiber was obtained from Shuangyang Chemical Factory (Beijing, China) and rinsed before use.

Before use all beakers, funnels, calibrated flasks, and other glassware were soaked in nitric acid (1+1) for 48 h.

Certified seawater CASS-4, NASS-5, SLEW-3 and river water SLRS-4 samples were purchased from the Institute for National Measurement Standards, National Research Council, Canada.

Instrumentation

A Plasma-Quad 3 (VG Elemental, Winsford, UK) inductively coupled plasma–mass spectrometer (ICP–MS) was used for determination of trace elements in water. The optimum instrumental conditions are given in Table 1. Indium was added as internal standard to monitor matrix effects and signal drift.

Immobilization procedure

Step 1

Rinsed fiber (10 g) and hydrazine hydrate (30%, v/v; 400 mL) were mixed in a 1-L flat-flange reaction vessel and reacted for 4 h at 94–96 °C in water bath. The hydrazine-modified fiber was isolated by filtration and washed with double-distilled deionized water. After washing, the fiber was dried and weighed.

Step 2

The hydrazine-modified fiber was further aminated by reaction with diethylenetriamine (50% v/v; 400 mL) for 6 h at 95 °C in water-bath, suction-filtered, and washed with ethanol (99.5%) and then with double-distilled deionized water until the pH was neutral. Then the fiber was dried and weighed.

Table 1 ICP–MS operating conditions

ICP	
Forward power	1350 W
Reflected power	<5 W
Coolant argon flow rate	14 L min^{-1}
Auxiliary argon flow rate	0.9 L min^{-1}
Nebulizer argon flow rate	0.8 L
Sample uptake rate	1.0 mL min^{-1}
Sampling depth	15 mm
Mass spectrometry	
Sampler (nickel) orifice	1.0 mm
Skimmer (nickel) orifice	0.7 mm
3rd stage pressure	1.7×10^{-1} mPa
Data acquisition	Range-scanning mode
Total acquisition time	60 s
Replication integrations per sample run	3
Element	Mass
Ag	107
Be	9
Cd	114
Co	59
Cr	52
Cu	65
Ni	60
Mn	55
Pb	208
Zn	66

Step 3

The diethylenetriamine-modified fiber was soaked in 400 mL of a solution of 20 g $NaNO_2$ in 0.2 mol L^{-1} acetic acid for 1 h at 0 °C. The product was filtered and rinsed with ice-cold double-distilled deionized water and then added to a 200 mL solution of 4 g of 8-hydroxyquinoline in 95% EtOH. After reaction for 1 h the diazo-coupled 8-hydroxyquinoline product was isolated by filtration and rinsed sequentially with 500 mL 0.5 mol L^{-1} NaOH, 500 mL H_2O, 500 mL 1.0 mol L^{-1} HCl, and three portions of 500 mL double-distilled deionized water. After rinsing the 8-hydroxyquinoline-modified fiber was dried and weighed.

Packing of 8-hydroxyquinoline-modified polyacrylonitrile fiber columns

Glass columns (4 mm i.d., 50 mm height) were plugged at the bottom with small amounts of glass-wool treated with 1% HNO_3. After thorough draining and rinsing with doubly-distilled deionized water 100 mg fiber, cut into lengths of approximately 1 mm and suspended in water, was slurry-packed into the columns which were then plugged with small amounts of glass wool inserted on the top of the fiber bed. The columns were rinsed first with 100 mL distilled water, then with 20 mL 2 mol L^{-1} HCl–0.1 mol L^{-1} HNO_3, and finally with doubly deionized distilled water until the pH of the eluate was neutral.

Fiber batch capacity

The chelating capacity of the 8-hydroxyquinoline-modified fiber was determined for each metal ion by a batch technique. Fiber (~50 mg) was equilibrated with each metal ion by shaking for 24 h at pH 6 in excess metal ion solution (50 mL, 50 μg mL^{-1}). The modified fiber was then separated from the solution by filtration and the concentration of the metal ions remaining in the solution was determined by ICP–MS.

Breakthrough study

Breakthrough studies were also chosen for characterization of the modified fiber, because they are more illustrative of dynamic column operation. Breakthrough curves were determined at different column flow rates using 1 μg mL^{-1} Cu(II) at the desired pH, adjusted by addition of high-purity aqueous ammonia or nitric acid. Eluate fractions were collected every 3 min by use of a fraction collector. The amounts of Cu(II) in each portion of eluate were determined by ICP–MS.

Preconcentration of trace elements from seawater and river water samples

Water samples (500 mL) were adjusted to pH 6, adjusted by addition of high-purity aqueous ammonia or nitric acid, then applied to the modified fiber column, at a flow rate of 5 mL min^{-1}, by use of a peristaltic pump. After washing with 50 mL doubly distilled deionized water, the trace elements retained in the column were eluted with 5 mL 2 mol L^{-1} HCl–0.1 mol L^{-1} HNO_3 at a flow rate of 1 mL min^{-1}.

Results and discussion

Optimum synthetic conditions

To immobilize as much 8-hydroxyquinoline as possible on the polyacrylonitrile fiber the synthetic conditions, e.g. reagent concentration, reaction temperature, and time, were optimized. The relative fiber weight increase was used as an indicator.

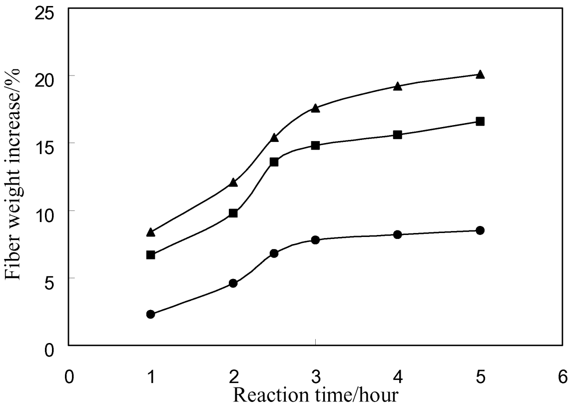

Fig. 1 Effect of reaction time, temperature, and concentration of hydrazine hydrate on the increase in the weight of the fiber (*circles*, 30% hydrazine hydrate, 90–92 °C; *squares*, 30% hydrazine hydrate, 94–96 °C; *triangles*, 40% hydrazine hydrate, 94–96 °C)

As shown in Fig. 1, the weight of the fiber increased sharply when the time of reaction with hydrazine hydrate was increased from 1 to 3 h, and then remained unchanged when the reaction time was further increased. Increasing the reaction temperature from 90–92 °C to 94–96 °C significantly improved the reaction efficiency. Increasing the concentration of hydrazine hydrate from 30% to 40% (v/v) led to a 5% increase in the mass of the fiber after reaction for 4 h. The best synthetic results were obtained with an initial hydrazine hydrate concentration of 40% (v/v) in the temperature range 94–96 °C. Because these reaction conditions are very close to the lower limits for the explosion of hydrazine hydrate gas mixtures, however [18], the concentration of hydrazine hydrate was limited to 30% (v/v). At the end of this procedure, the color of the white fiber turned to pale yellow.

Figure 2 reveals that the reaction between the hydrazine-modified fiber and diethylenetriamine depends

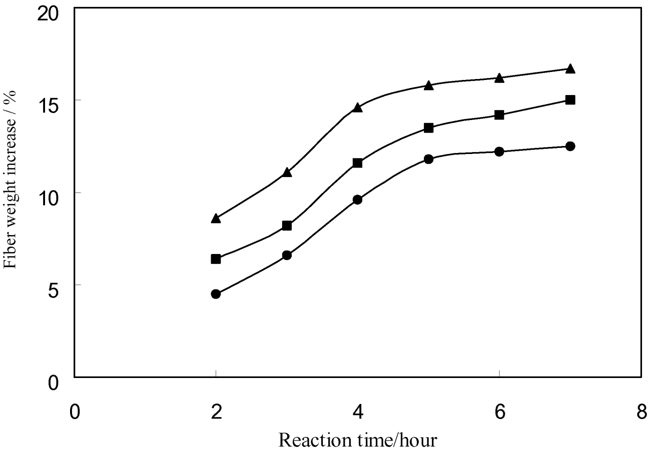

Fig. 2 Effect of reaction time, temperature, and concentration of diethylenetriamine on the increase in the weight of the fiber (*circles*, 30% diethylenetriamine, 90 °C; *squares*, 50% diethylenetriamine, 90 °C; *triangles*, 50% diethylenetriamine, 95 °C)

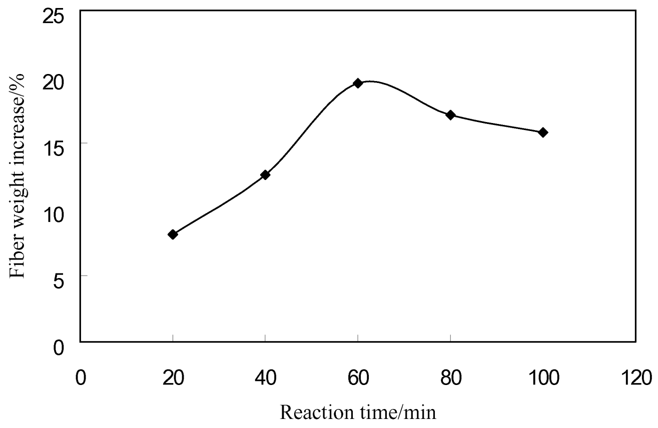

Fig. 3 Effect of reaction time between fiber and $NaNO_2$ on the increase in the weight of the fiber

strongly on reaction temperature, time, and the concentration of diethylenetriamine. Increasing these resulted in a large increase in the weight of the fiber. For rapid synthesis 50% (v/v) diethylenetriamine and 95 °C reaction temperature were chosen, and the reaction time was fixed at 6 h, after which the increase in the weight of the hydrazine-modified fiber was 13.8%, and the color of the fiber was red–orange.

As shown in Fig. 3, when the reaction time with $NaNO_2$ was increased from 20 min to 60 min, the fiber weight increased but there was no further fiber weight increase, and even a slight decrease, possibly because of diazo decomposition [3], when the reaction time was prolonged to 2.5 h. Because such losses should be avoided, the reaction time between diethylenetriamine modified fiber and $NaNO_2$ should not exceed 1 h. After reaction and washing with cold water for short time the fiber must be immersed in ethanolic 8-hydroxyquinoline solution immediately to produce the red–brown 8-hydroxyquinoline-modified polyacrylonitrile fiber.

Fiber batch capacity test

A batch technique was chosen to determine which metal ions could be sorbed. By following the procedure described in the experimental section the capacity of Ag, Au, Be, Bi, Co, Cd, Cr(III), Cu, In, Mn, Ni, Pb, Pd, Pt, and Zn at pH 6 was determined; the results are shown in Table 2.

Table 2 Batch capacity (µmol g^{-1})

Element	Batch capacity	Element	Batch capacity
Ag	162.5	Au	111.9
Be	108.8	Bi	98.6
Co	212.5	Cd	208.3
Cr(III)	167.3	Cu	302.8
In	156.3	Mn	323.5
Ni	177.9	Pb	138.5
Pd	105.7	Pt	98.6
Zn	315.6		

Breakthrough capacity

The breakthrough capacity is affected by many factors, for example pH, sample flow rate, etc. It is useful to evaluate how the effectiveness of the 8-hydroxyquinoline-modified polyacrylonitrile fiber is altered by changing one condition while holding the others constant. The breakthrough capacity demonstrates the suitability for preconcentration of trace metals. The effects of pH, sample flow rate, alkali and alkaline earth cations on the breakthrough capacity and on fiber stability are discussed in detail below. The ratio of Cu(II) concentration in the eluate to that in initial solution (C/C_0) was used as an indicator.

Effect of pH on breakthrough capacity

The effect of pH from 3 to 8 on Cu(II) breakthrough capacity was studied at a flow rate of 5 mL min^{-1} for a column packed with 100 mg fiber (Fig. 4). It is apparent that the breakthrough capacity (95% of analytes adsorbed by the fiber) at pH 8 was 29 mol, whereas at pH 3 it decreased to 10 mol, illustrating the competition of protons for exchange sites at low pH. At pH 6 the breakthrough capacity was 24.6 mol; because the amount of fiber packed in the column was 100 mg the capacity of the 8-hydroxyquinoline-modified polyacrylonitrile fiber for Cu(II) was 246 mol g^{-1} at this pH. The profiles of these curves were not significantly different, indicating that film- and particle-diffusion control might be rate limiting under these experimental conditions.

Effect of sample flow rate on breakthrough capacity

Figure 5 shows the effect of flow rate on breakthrough capacity at pH 6. It is apparent that increasing the flow rate

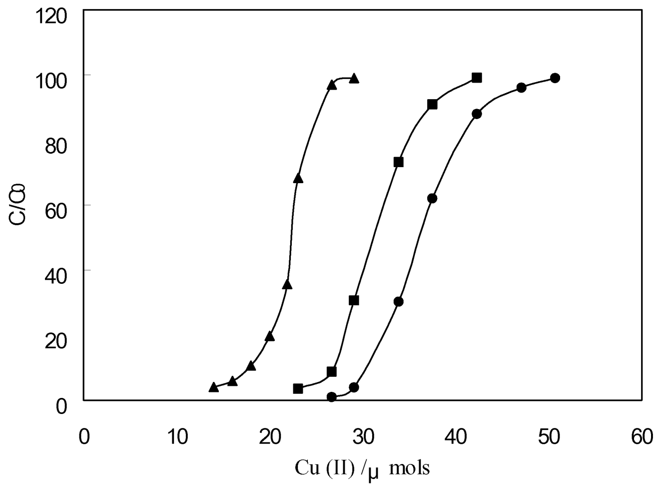

Fig. 4 Effect of pH on breakthrough capacity (*circles*, pH 8.0; *squares*, pH 6.0; *triangles*, pH 3.0)

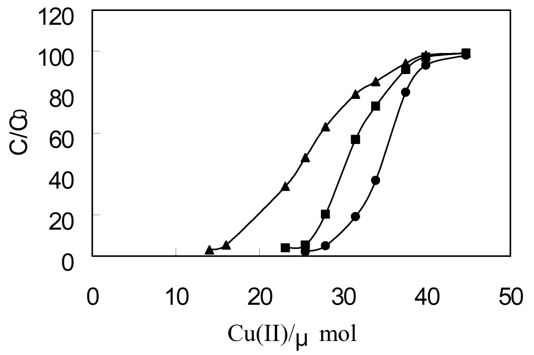

Fig. 5 Effect of sample flow rate on breakthrough capacity (*circles*, 2 mL min^{-1}; *squares*, 5 mL min^{-1}; *triangles*, 8 mL min^{-1})

from 2 to 8 mL min^{-1} reduced the breakthrough capacity of Cu(II) from 278 to 200 mol g^{-1}.

Although it is difficult to compare the breakthrough capacity directly with results from other workers, because of different experimental conditions such as column dimensions, pH, sample flow rate, etc., some estimates can be made. Landing et al. [12] reported 294 mol g^{-1} Cu(II) as the breakthrough capacity of 8-hydroxyquinoline-modified vinyl polymer agglomerate (pH 6.3, sample flow rate 0.2 mL min^{-1}). Lofthouse et al. [22] reported a batch capacity value of 138 μmol g^{-1} and a dynamic capacity of 102 μmol Mn(II) g^{-1} for 8-hydroxyquinoline immobilized on a microporous silica frit. Compared with batch capacities reported in the literature for 8-hydroxyquinoline immobilized on other substances this value is greater than those reported by Marshall and Mottola [23], 185 μmol Cu(II) g^{-1}, Nelms et al. [24], 86 μmol Cu(II) g^{-1}, Sturgeon [25], 61 μmol Cu(II) g^{-1}, Daihi [10], 10.4 μmol Cu(II) g^{-1}, and that of our previous product, 71.5 μmol Cu(II) g^{-1} [21]. Compared with those of other ion-chelating substances reported recently, the breakthrough capacity of our new material is equivalent to that of tiron-functionalized Amberlite XAD-2, 215 μmol Cu(II) g^{-1} [26], and greater than that of chromotropic acid-modified Amberlite XAD-2, 143.8 μmol Cu(II) g^{-1} [27], diethylenetriamine polymer, 80 μmol Cu(II) g^{-1} [28], and 1-(2-pyridylazo)-2- naphthol immobilized on alumina, 23.7 Cd(II) μmol g^{-1} [29].

Effect of alkali and alkaline earth cations on breakthrough capacity

To illustrate the possibility of concentrating trace metals from high salt matrices by use of immobilized 8-hydroxyquainoline the breakthrough capacity of Cu(II) was compared in the presence or absence of 20,000, 500, 2500, and 500 mg L^{-1} of $Na^{+,}$ K^{+}, Mg^{2+}, and Ca^{2+}, respectively, as the chlorides. The results are shown in Fig. 6. In the presence of high concentrations of alkali and alkaline earth cations the breakthrough capacity of Cu(II) was reduced from 246 to 198.6 mol g^{-1}. This breakthrough capacity was, nevertheless, still high enough for concentration of trace elements from real water samples. The 8-hydroxyquainoline-modified fiber could also effectively separate matrices.

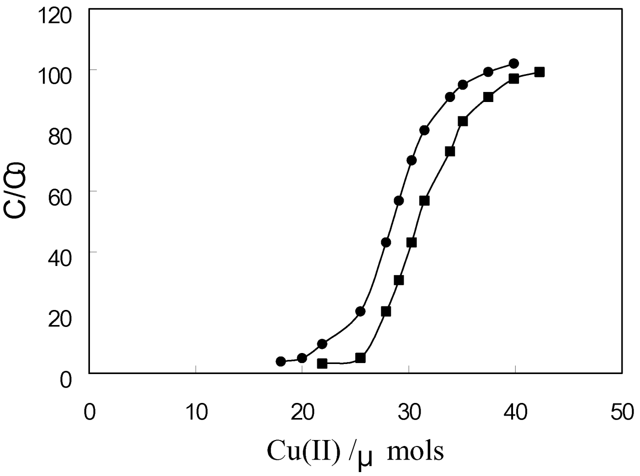

Fig. 6 Effect of alkali and alkaline earth elements on breakthrough capacity (*circle*, with matrix ions; *squares*, without matrix ions)

Fiber stability

Breakthrough capacity studies were also chosen for determination of the chemical stability of the modified fiber (pH 6.0, flow rate 5 mL min^{-1}). Copper(II) was used as the indicating species (1 μg mL^{-1}). As shown in Fig. 7, after treatment with acid (2 mol L^{-1} HCl–0.1 mol L^{-1} HNO_3) for 2 and 48 h, the breakthrough capacity was 24.4 and 24.2 mol, respectively, indicating that the fiber was very stable in acidic solution.

Similarly, soaking in 0.5 mol L^{-1} NaOH for 2 h had little effect on the breakthrough capacity (Fig. 8). After treatment for 48 h, despite obvious reddish coloration of the basic solution, indicating base-catalyzed hydrolysis, the breakthrough capacity increased to 33.6 mol, possibly because of the formation of carboxyl groups [18].

Blank and detection limits

Blank values for analyte determinations were obtained by performing the preconcentration procedure using 500 mL

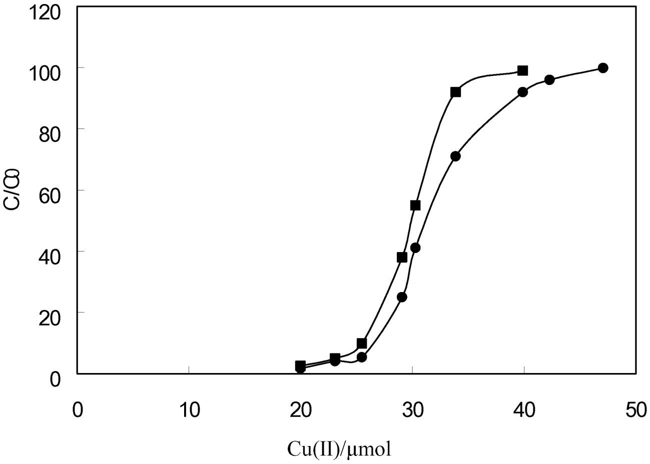

Fig. 7 Effect of acid treatment on breakthrough capacity (*circles*, 2-h acid treatment; *squares*, 48-h acid treatment)

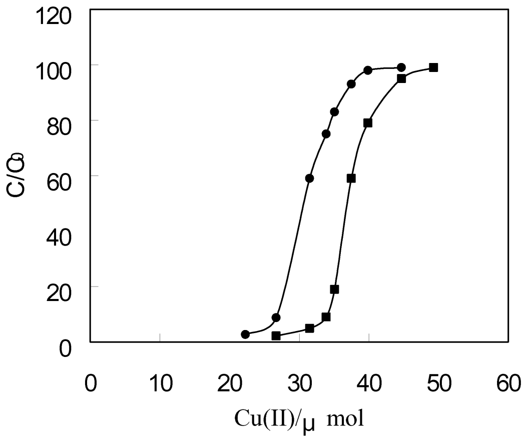

Fig. 8 Effect of treatment with alkali on breakthrough capacity (*circles*, 2-h alkali treatment; *squares*, 48-h alkali treatment)

Table 3 Blanks and detection limits (ng L^{-1})

Element	Blank		Detection limit	
	One blank solution	Eleven blank solutions	One blank solution	Eleven blank solutions
Ag	9.4	10.8	5.6	5.8
Be	17.1	31.4	51.6	52.5
Cd	4.1	6.4	6.1	6.4
Co	2.9	3.0	0.4	1.0
Cu	4.8	9.3	9.8	11.6
Ni	310.0	319.7	27.3	29.8
Mn	22.9	76.0	121.5	129.1
Pb	41	48.8	12.6	13.6
Zn	101.2	129.8	88.7	89.3

doubly-distilled deionized water as a sample and 5 mL 2 mol L^{-1} HCl–0.1 mol L^{-1} HNO_3 as eluent. The detection limits for the method were calculated on the basis of three times the standard deviation of 11 runs of one blank solution or that from one run of 11 blank solutions. The detection limits and blank values are shown in Table 3. It is clearly apparent that the blank and detection limit values of two approaches were similar in magnitude. Compared with the concentrations of analytes present in seawater and river water samples (Table 4) all analyte concentrations in the real samples are much greater than the detection limits after 100-fold preconcentration.

Determination of trace metals in water samples

From the breakthrough and batch capacity studies it is apparent that the 8-hydroxyquinoline-modified polyacrylonitrile fiber has a relative high capacity for many metal ions, and its kinetic characteristics are satisfactory. The newly 8-hydroxyquinoline-modifed polyacrylonitrile fiber was applied to the determination of trace metals in certified reference materials NASS-5, CASS-3, CASS-5 seawater, and SLRS-4 river water. The results shown in Table 4 are mean values±standard deviations. There is a good agreement between the data obtained by the recommended method and the certified values.

Table 4 Determination of trace metals in the certified seawater (CASS-4, NASS-5, and SLEW-3) and river water(SLRS-4) samples (μg L^{-1})[a]

Element	CASS-4		NASS-5	
	Measured	Certified	Measured	Certified
Cd	0.029±0.002	0.026±0.003	0.021±0.002	0.023±0.003
Co	0.026±0.002	0.026±0.003	0.010±0.001	0.011±0.003
Cu	0.638±0.038	0.592±0.055	0.269±0.023	0.297±0.046
Ni	0.324±0.020	0.314±0.030	0.218±0.020	0.253±0.028
Mn	2.75±0.021	2.78±0.19	0.962±0.046	0.919±0.057
Pb	0.105±0.0012	0.0098±0.0036	0.010±0.001	0.008±0.005
Zn	0.372±0.030	0.381±0.057	0.099±0.010	0.102±0.039
	SLEW-3		SLRS-4	
Ag	0.003±0.0003	(0.003)[a]	–	–
Be	–	–	0.006±0.0005	0.007±0.002
Cd	0.050±0.003	0.048±0.004	0.14±0.01	0.12±0.002
Co	0.043±0.002	0.042±0.010	0.035±0.003	0.033±0.006
Cu	1.49±0.13	1.55±0.12	1.87±0.09	1.81±0.08
Ni	1.26±0.06	1.23±0.07	0.63±0.05	0.67±0.08
Mn	1.60±0.13	1.61±0.22	3.20±0.11	3.37±0.18
Pb	0.0087±0.0007	0.0090±0.0014	0.086±0.003	0.086±0.007
Zn	0.210±0.020	0.201±0.037	0.98±0.07	0.93±0.10

[a] Three measurements

Conclusion

In the work discussed in this report a rapid synthetic route has been devised for effective immobilization of 8-hydroxyquinoline on the polyacrylonitrile fiber. Compared with other immobilized materials this product has the following features:

1. ease of synthesis;
2. the breakthrough and batch capacity of this fiber are greater than for most of other 8-hydroxyquinoline-modified materials reported in the literature;
3. stability in acidic or alkaline conditions is satisfactory; and
4. the mechanical strength is higher and the material can be stored and applied conveniently.

The effectiveness of the concentration of multi-trace metals from complicated matrices was verified and the results confirmed that the modified fiber is suitable for determination of trace metals in certified seawater and river water samples, indicating the modified fiber has good prospects.

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