Synthesis and characterization of poly(acrylamino-phosphonic-carboxyl-hydrazide) chelating fibre

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Abstract

The poly(acrylamino-phosphonic-carboxyl-hydrazide) chelating ion exchange fibre was prepared by the amination and phosphorization reaction of the hydrazine-modified polyacrylonitrile fibre. The structure of the chelating fibre and the same fibre saturated by Cu(II) and Ag(I) ions was investigated by IR spectrometer in detail. In addition, the crystalline and surface characteristics of the chelating fibre were determined by X-ray diffraction and SEM. The higher binding capacities of the fibrous sorbent for Cu(II), Pb(II), Zn(II), Co(II), Ni(II), Hg(II), Cd(II), Mn(II), Cr(III) and Ag(I) and the effect of pH value on adsorption of the chelating fibre for Cu(II) and Hg(II) ions were examined. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Poly(acrylamino-phosphonic-carboxyl-hydrazide) chelating fibre; Synthesis; Characterization; Adsorption

1. Introduction

The determination of trace toxic metals in nature water and waste water is important from two different aspects. The first is the inorganic pollution of these waters in which metals have reached concentrations which may be deleterious to aquatic life and ultimately man. The second consideration is that of micronutrient regimes for various life forms, for example essential trace elements such as copper, molybdenum, iron, and manganese are present in sea water at very low levels. These are

readily depleted resulting in large areas of the ocean which are aquatic equivalents of barren deserts. Therefore, the trace metal contents in natural waters and waste water must be monitored to determine whether the concentration have reached toxic proportions or have been depleted below the micronutrient requirement levels. Thus, the requirement for polymeric chelating sorbents in the fields of analytical chemistry and environmental protection has been risen substantially at present.

The ion exchange chelating fibre has been developed as highly effective sorbents following the ion exchange chelating resins. Fibrous ion exchangers have been characterized by the high

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specific surface, which is larger by about two order of magnitude than that of a gel-structure granular ion-exchanger or 5–6 times higher than the surface of a porous copolymer. The fibrous sorbents have good kinetic properties, and can conveniently be applied in different shapes, such as films, filters, tubes, etc. Therefore, fibrous sorbents have attracted great interest in recent years [1–5].

The principal synthetic methods of ion exchange chelating fibre are the copolymerization of monomeric (polymeric) compounds containing ion exchange chelating groups with fibre-forming polymers or monomers and the transformation of the active groups on the initial fibre as a carbon skeleton. The latter method has some advantages, for instance, the ready-made skeleton, varieties of fibres, lower price and simple synthetic step etc.

In this paper, the newly developed sorbent, poly(acrylamino-phosphonic-carboxyl-hydrazide) chelating fibre, was prepared. The surface and crystalline characteristics of the chelating fibre were investigated, the structure analysis of the chelating fibre and the same fibre loaded by Cu(II) and Ag(I) ions was carried out. The binding capacities for heavy metals were reported.

2. Experimental

2.1. Reagents

The polyacrylonitrile fibre (PANF, a common commercial product) was obtained from a Chinese chemical factory. All reagents used were analytical-reagent grade except specified one. The purest available metal salts and distilled water were used throughout the procedure.

0.1 and 0.015 mol/l stock solutions of Cu(II), Cd(II), Co(II), Zn(II), Mn(II), Pb(II), Ni(II), Ag(I) and Cr(III) were prepared by dissolving appropriate quantities of $\text{CuCl}_2 \cdot \text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, ZnCl_2 , $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, AgNO_3 and

$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, respectively, in 500 ml distilled water, 30 ml concentrated nitric acid was added, and the solution was diluted to 1 l with distilled water. Similarly, appropriate amount of HgSO_4 was dissolved in 500 ml glacial acetic and diluted to 1 l with distilled water.

2.2. Apparatus and instruments

IR spectrums were obtained with a Model 5ZDX FTIR spectrometer (Nicolet). ST-02 elements analyzer and DU-650 spectrophotometer (Beckman) were respectively used for the determination of nitrogen, oxygen and phosphorous content of the fibrous sorbents. Z-6100 atomic absorption spectrometer was used for the determination of all metals. The pH value of solution was adjusted with a Model PHS-3C pH meter. The determination of X-ray diffraction spectrums was performed by APD-10 X-ray diffractometer (Philips). Model S-520 scanning electron microscope (Hitachi) was used to investigate the surface characteristics of the chelating fibre. A synthetic reaction was performed in a three-necked flask.

2.3. Synthesis of poly(acrylamino-phosphonic-carboxyl-hydrazide) chelating fibre

The synthetic reaction was carried out as following three stages.

2.3.1. Step 1

The hydrazine-modified polyacrylonitrile fibre was obtained according to the method of the literature [6], and the weight increase of the product was about 5–8%.

2.3.2. Step 2

An amount of dry hydrazine-modified polyacrylonitrile fibre and diethylenetriamine of (1 + 40) proportion were mixed in a one-litre three-necked reaction vessel. The mixture was heated to $95^\circ\text{C} \pm 1$ for 5–10 h. Afterward the mixture was cooled, suction-filtered, sequentially washed with distilled water until the pH

value of the washing was neutral, and then dried at 60–65°C overnight. The fibre-aminated was obtained.

2.3.3. Step 3

The final product, poly(acrylamino-phosphonic-carboxyl-hydrazide) chelating fibre, expressed as PAAP-2, was prepared by the reaction of the above fibre-aminated with phosphorous acid of (1 + 40) proportion for 6 h at 85–95°C, suction-filtered, washed with distilled water and dried at 60–65°C overnight.

2.4. Binding capacity

The binding capacities of the poly(acrylamino-phosphonic-carboxyl-hydrazide) chelating fibre for heavy metal ions were determined by batch technique. Dried samples (0.100 g each) of the fibrous ion exchanger were equilibrated by shaking for 24 h at 25°C ± 1 in 10 ml metal ion solution. The concentrations of metal ions were 0.015 mol/l, and the metal solutions were adjusted to pH 4.5 for Cu(II), Pb(II) and Cr(III); 5.5 for Ni(II) and Co(II); 5.0 for Zn(II); 5.2 for Cd(II); 6.0 for Mn(II), Hg(II) and Ag(I) with diluted ammonia water prior to equilibration.

2.5. Effect of pH value on adsorption and distribution coefficient

0.100 g of the PAAP-2 chelating fibre samples were equilibrated by shaking for 24 h at 25 ± 1°C in 10 ml of 0.001 mol/l Cu(II) and Hg(II) ion solutions. The metal solutions were adjusted to pH 1.0–7.0 with diluted ammonia water prior to equilibration.

2.6. Investigation of IR spectrum

The PAAP-2 chelating fibre lone and the chelating fibres saturated with Cu(II) or Ag(I), which were obtained through the determination method of binding capacity, were prepared in KBr pellets, and their IR spectra were determined.

3. Results and Discussion

3.1. Crystalline and surface properties of the PAAP-2 chelating fibre

The result of X-ray diffraction spectrum (see Fig. 1) shows that the PANF exhibits a good crystalline property, as shown in Fig. 1a, the crystallinity of which reaches to 55% according to the calculation method of the literature [7]. The crystalline peak for the PAAP-2 chelating fibre, however, disappears completely (see Fig. 1b). This phenomenon is mainly attributed to two explanations. One is that the polar interaction between molecule decreases with reaction processing; the other is that the activity of molecule chain is limited due to the formation of cyclic structure during the synthetic reaction. These two causes result in the decrease of regular degree or crystallinity of the PAAP-2 chelating fibre. Each fibre has its own paracrystalline region. When the reaction temperature is higher than that at which the paracrystalline region of the fibre is destroyed, the crystallinity of the fibre is decreased greatly and its mechanical property begins to be inferior. But the fibre with lower crystallinity has quite softness and elasticity. To some extent, the formation of cyclic structure makes up for effect of crystallinity on the mechanical strength of the fibre.

From SEM photographs of the PANF and the PAAP-2 chelating fibre (see Fig. 2), it is shown that the surface characteristic of the PAAP-2 chelating fibre has not obvious difference compared with that of the PANF. The crackle on the surface of the PAAP-2 chelating fibre has not been observed. Therefore, the chelating fibre still has a favourable property in general.

3.2. Structure of the PAAP-2 chelating fibre

The IR spectra of the PANF, the hydrazine-modified fibre, the fibre-aminated and the PAAP-2 chelating fibre are shown in Fig. 3.

The mechanism of interaction of hydrazine

Fig. 1. X-ray diffraction spectra of PANF (a) and PAAP-2 chelating fibre (b).

Fig. 2. Scanning electron microscope photographs of PANF (a) and PAAP-2 chelating fibre (b).

Fig. 3. IR spectra of PANF (a), the hydrazine-modified PANF (b), the fibre-aminated (c) and the PAAP-2 chelating fibre (d).

with PANF has not yet been conclusively established. The IR spectrum of the PANF (Fig. 3, spectrum a) shows the absorption peaks of stretching vibration at 2242 cm^{-1} ($\text{C}\equiv\text{N}$), 1736 cm^{-1} ($\text{C}=\text{O}$ of ester group), and a broad absorption band in the $3600\text{--}3400\text{ cm}^{-1}$ ($-\text{OH}$) [8], which explains the PANF as a tripolymer [9]. In the spectrum b of Fig. 3, the absorption band at

$3600\text{--}3400\text{ cm}^{-1}$ is shifted to shorter wavenumber of $3500\text{--}3400\text{ cm}^{-1}$, and the intensity of the peak also increases greatly. This behaviour corresponds to stretching vibration of N-H group. The broad absorption band in the region of $1652\text{--}1630\text{ cm}^{-1}$ is probably due to stretching vibration of $\text{C}=\text{N}$ group. The new broad peak at 1560 cm^{-1} is contributed to the

overlapping of C–N stretching vibration with N–H bending vibration [10]. It is also observed that the intensity of the peaks at 2242 cm^{-1} ($\text{C}\equiv\text{N}$) and 1736 cm^{-1} ($\text{C}=\text{O}$) reduces obviously. These data support the argument that the cross-link of hydrazine with PANF leads to the formation of hydrazide group and the decrease of the content of nitrile and ester groups [8,11,12]. The complete disappearance of the peak at 1736 cm^{-1} and the existence of characteristic absorption in $3460\text{--}3420\text{ cm}^{-1}$ (N–H), 1659 cm^{-1} ($\text{C}=\text{O}$, $\text{C}=\text{N}$) and 1560 cm^{-1} (N–H) in Fig. 3c, conform that the reaction process of the hydrazine-modified PANF with diethylenetriamine occurs in ester group, and at the same time, the nitrile group may be transformed to carboxyl in the presence of amine. According to the IR spectrum d of Fig. 3 and the literature [13,10], the introduction of phosphonic group is indicated by stretching vibration of $\text{P}=\text{O}$ at $1230\text{--}1181\text{ cm}^{-1}$ and $\text{P}\text{--}\text{O}$ group at $1054\text{--}1019\text{ cm}^{-1}$, 920 cm^{-1} .

Therefore, on the base of literature data and the structure analysis of the chelating fibre, we can assume that the composition of the PAAP-2 chelating fibre includes carboxyl, amino, phosphonic and hydrazide groups. Three synthesis can be briefly expressed as shown in Scheme 1. The results of element analysis shown in Table 1 indicate the subsequent loss of nitrogen and the increase of oxygen during the reaction process. For this point, there are several explanations. The formation of cyclic structure in different reaction step of the fibre and the conversion of the nitrile groups would correspond to decrease of the nitrogen content. The hydrolysis of the nitrile groups may result in the increase of oxygen content during the conversion of the fibre [14,15].

3.3. IR spectrum analysis of the metal complexes of PAAP-2 chelating fibre with Cu(II) and Ag(I)

Fig. 4 shows the IR spectra of the PAAP-2

chelating fibre treated by 1% NaOH solution and the same fibre saturated with Cu(II) or Ag(I). The absorption peaks in Fig. 4 can be assigned as in Table 2 based on the literature [10,16,17]. In comparison to Fig. 3d, the appearance of the sharp, but weak absorption peak at 979 cm^{-1} and the increase of the band intensity in $1150\text{--}1000\text{ cm}^{-1}$ of Fig. 4a are attributed to the characteristic absorption of $\text{--P}(\text{:O})(\text{ONa})_2$ group transformed from $\text{--P}(\text{:O})(\text{OH})_2$ group [16]. After the PAAP-2 chelating fibre (Na-type) is coordinated with Cu(II), the original peaks at 3440 , 1590 , $1118\text{--}1089$ and 910 cm^{-1} are displaced to 3410 , 1580 , $1100\text{--}1061$ and 913 cm^{-1} , while the absorption band at 979 cm^{-1} disappears completely. These phenomena are due to the coordination of the lone-pair electron of the nitrogen atom in N–H with Cu(II), resulting in an incremental change of the bond force constant of N–H [16,17] and the exchange reaction of Na^+ in $\text{--P}(\text{:O})(\text{ONa})_2$ with Cu(II). In addition, it is observed that the peak intensity at 1404 cm^{-1} for the Cu(II)–PAAP-2 complex increases greatly. The characteristic absorption at 1404 cm^{-1} , corresponding to stretching vibration of --CH_2 , is contributed to the existence of the active --CH_2 group in metal complex of PAAP-2 chelating fibre with Cu(II) [10]. This further shows that the coordination of Cu(II) ion with nitrogen atom occurs in the structure of $\text{--NH--CH}_2\text{--P}(\text{:O})(\text{ONa})_2$, which results in the formation of $\text{--N}^+\text{--CH}_2\text{--}$ and the activation of --CH_2 . The hypothetical structure can be illustrated by Scheme 2.

For Ag(I)–PAAP-2 complex (see Fig. 3c), the IR spectral behaviour is quite similar to that of Cu(II)–PAAP-2 complex. The stretching vibration of NH_2 , $\text{P}=\text{O}$, $\text{P}\text{--}\text{O}$ and the bending vibration of NH , NH_2 respectively shift to lower wavenumbers: 3430 , $1109\text{--}1059$, 908 and 1563 cm^{-1} compared with the PAAP-2 chelating fibre. These data verify that Ag(I) coordinates with PAAP-2 chelating fibre through amino and phosphonic groups. The further research on the complex mechanism of metal ion with the PAAP-2 chelating fibre is still under study.

Scheme 1. Three-step synthesis of PAAP-2 chelating fibre.

Table 1

The amount of nitrogen, oxygen and phosphorus in different reaction products

	N (%)	O (%)	P (%)
PANF	23.4	7.18	—
Hydrazine-modified fibre	25.71	4.33	—
Fibre-aminated	19.84	13.23	—
PAAP-2 chelating fibre	16.17	19.18	3.99

3.4. Adsorption properties of PAAP-2 chelating fibre for metal ions

The several metal ions are absorbed simultaneously by the chelating fibre due to the existence of multi-functional groups with different coordination characteristics such as carboxyl, amino, phosphonic and hydrazide groups.

Fig. 4. IR spectra of PAAP-2 chelating fibre treated by 1% NaOH solution (a), the same fibre saturated with Cu(II) (b) and Ag(I) (c).

The capacities of the PAAP-2 chelating fibre for heavy metal ions are listed in Table 3. The specific capacities decreases as the following sequence: Ag(I) > Pb(II) > Cu(II) > Ni(II) > Zn(II) > Cd(II) > Co(II) $\approx$ Hg(II) > Mn(II) > Cr(III). Due to the protonation and deprotonation properties of the groups of the ion exchanger, its metal uptake behaviour is effected by the pH value. The binding capacity of the chelating ion exchange fibre for each metal ion depends on the affinity of the functional group for the metal ion. Usually, the strength of the

affinity can be expressed as the complex formation constant.

The comparison of the binding capacities of several chelating sorbents is also listed in Table 3. With the exception of chromium, the PAAP-2 chelating fibre surpasses the other chelating ion exchangers in its ability to bind the listed metal ions. The remarkable result is the higher adsorption capacities for silver, lead, copper and mercury.

The pH value is one of the most important factors in adsorption experiment, and it influ-

Table 2

Classification of IR spectra of the PAAP-2 chelating fibre (Na-type) and the fibre saturated with Cu(II) and Ag(I)

Number	Assignment ^a	Wavenumber (cm ⁻¹)		
		PAAP-2 (Na-type)	PAAP-2–Cu(II)	PAAP-2–Ag(I)
1	$\nu(\text{NH}_2)$	3440	3410	3430
2	$\nu(\text{NH})$	–	3200	–
3	$\nu(\text{CH}_2)$	2940	2920	2930
4	$\nu(\text{CH})$	2890	2860	2860
5	$\nu(\text{C}=\text{N}, \text{C}=\text{O})$	1658–1640	1652–1635	1659–1639
6	$\delta(\text{NH}, \text{NH}_2)$	1590	1580	1563
7	$\delta(\text{CH})$	1451	1452	1445
8	$\delta(\text{CH}_2)$	1404	1404	1401
9	$\delta_s(\text{CH}_2)$	1385	–	1382
10	$\nu(\text{P}=\text{O})$	1118–1089	1100–1061	1109–1059
11	$\nu(\text{P}=\text{ONa})$	979	–	955
12	$\nu(\text{P}=\text{O})$	910	913	908
13	$\delta(\text{NH})$	778	777	786
14	$\delta(\text{N}=\text{C}=\text{O})$	558	554	555

^a ν = stretching vibration; δ = bending vibration; δ_s = scissor vibration.

Scheme 2. Proposed structure of the Cu(II)–PAAP-2 complex.

ences the surface structure of sorbents, the formation of metal ions and the interaction between sorbents and metal ions. Therefore, the pH value dependence of the adsorption for metal ions is examined in detail. Fig. 5 shows the curves of adsorption percentage of PAAP-2 chelating fibre for Cu(II) and Hg(II) as function of the pH value. For Cu(II), the degree of adsorption is constant at 99% above pH 3.0, and

decreases rapidly in the pH range 1–3, while Cu(II) ion is scarcely adsorbed below pH 1.0. But, the strong difference is observed for Hg(II) ion. The adsorption percentage for Hg(II) ion is still 95% even at pH 1.5. With the increase of pH value, the degree of sorption for Hg(II) ion reaches to above 99%. The insensitiveness of Hg(II) ion for pH value is attributed to the presence of multi-groups in the PAAP-2 chelating fibre. At low pH value, the protonation of amino-group results in the decrease of the affinity of nitrogen atom for Hg(II) ion, but the phosphonic group of the chelating fibre, having a good ionization character, can complex with Hg(II) under strong acidic solution [19].

The distribution coefficient (D) at a pH value shows the affinity of ion exchange sorbent for metal ions. The Table 4 lists the distribution

Table 3

Specific binding capacity Q (mmol/g) of several chelating sorbents for metal ions

Metals	Cu(II)	Cd(II)	Cr(III)	Co(II)	Pb(II)	Hg(II)	Ni(II)	Mn(II)	Ag(I)	Zn(II)
pH	4.5	5.2	4.5	5.5	4.5	6.0	5.5	6.0	6.0	5.0
PAAP-2	1.47	1.36	0.76	1.25	1.55	1.25	1.40	1.17	2.12	1.39
pH	5.0	5.0	–	5.0	5.0	5.0	5.0	–	–	5.0
PAADX [18]	1.45	0.19	–	0.34	0.72	1.07	0.40	–	–	0.38
pH	4.0	6.0	4.0	6.0	4.5	1.5	6.0	–	–	6.0
MPANF [6]	1.33	1.30	0.96	1.02	0.98	0.63	0.95	–	–	1.03

PAADX = poly(acrylamidoxime) chelating fibre.

MPANF = hydrazine-modified polyacrylonitrile fibre.

Fig. 5. Effect of pH value on the adsorption of PAAP-2 chelating fibre for Cu(II) and Hg(II).

Table 4

Distribution coefficients (D) of PAAP-2 chelating fibre for Cu(II) and Hg(II)

Metal complex	pH value					
	2.0	3.0	4.0	5.0	6.0	6.5
PAAP-2–Cu(II)	6.37×10^2	2.12×10^3	–	1.12×10^4	–	5.39×10^3
PAAP-2–Hg(II)	5.10×10^3	5.37×10^3	1.12×10^4	1.83×10^4	1.97×10^4	–

Conditions: solution volume = 10 ml; the fibre amount = 0.100 g; shaking time = 24 h; temperature = 25°C; concentration of metal ions = 0.001 mol/l.

coefficient of the PAAP-2 chelating fibre for Cu(II) and Hg(II). At a low pH value, the D values for Cu(II) are lower, while for Hg(II), are above 10^3 in the studied range of pH value. This result exhibits that the PAAP-2 chelating fibre has a higher affinity for Hg(II) than for Cu(II).

4. Conclusion

A chelating fibre containing carboxyl, amino, phosphonic and hydrazide groups has been prepared readily. Comparative investigations of the spectroscopic properties of the fibres obtained in different reaction steps and poly-(acrylamino phosphonic-carboxyl-hydrazide) chelating fibre loaded with Cu(II) and Hg(II)

result in an attempt to explain the interaction between Cu(II) and Hg(II) with the chelating fibre, and it is pointed out that the coordination of Cu(II) and Hg(II) ions with the PAAP-2 chelating fibre occurs through the phosphonic and the nitrogen atom of amino group. With synthetic reaction processing, the surface property of the final product is still favourable, though the crystalline characteristic of the chelating fibre begins to be inferior.

The newly developed fibrous sorbent has high adsorption capacities for Cu(II), Pb(II), Zn(II), Co(II), Ni(II), Hg(II), Cd(II), Mn(II), Cr(III) and Ag(I). The adsorption of the chelating fibre for Cu(II) is greatly influenced by the pH value, while Hg(II) exhibits an insensitiveness for the pH value.

Therefore, the newly developed chelating

fibre might be an effective tool for removal and preconcentration of heavy metals from natural waters and industrial effluents.

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