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<tr>
<td><strong>Citation</strong></td>
<td>Reactive and Functional Polymers, 70(8): 508-515</td>
</tr>
<tr>
<td><strong>Issue date</strong></td>
<td>2010-08</td>
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<tr>
<td><strong>Type</strong></td>
<td>Journal Article</td>
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<td><strong>URL</strong></td>
<td><a href="http://hdl.handle.net/2298/19738">http://hdl.handle.net/2298/19738</a></td>
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<td>© 2010 Elsevier Ltd.</td>
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Preparation of bifunctional chelating fiber containing iminodi(methylphosphonate) and sulfonate and its performances in column-mode uptake of Cu(II) and Zn(II)

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ABSTRACT

The bifunctional chelating fiber, FNPS, was prepared from vinylbenzyl chloride (CMS) grafted polyethylene-coated polypropylene fiber (PPPEf-g-CMS). In addition to the primary iminodi(methylphosphonate) chelating groups, FNPS has sulfonate groups as secondary functional group. FNPS was prepared by the following four steps. First, PPPEf-g-CMS was reacted with potassium phthalimide to substitute chlorine atoms in PPPEf-g-CMS with phthalimide groups. Second, sulfonate groups were introduced into the phenyl groups of benzyl moieties on the grafted polymer chains by the reaction with 95% sulfuric acid. Third, phthalimide moieties were hydrolyzed with ethanol solution of hydrazine hydrate to give the primary amino groups at the end of benzyl moieties on the grafted chains. Finally, these primary amino groups were converted into iminodi(methylphosphonate) groups by Mannich condensation reaction, in which the precursory fiber was reacted with large excess phosphorous acid and paraformaldehyde in 6 M hydrochloric acid media under the refluxed conditions for 6 h. The sulfonate and iminodi(methylphosphonate) groups in the resulting FNPS were identified by FT-IR spectroscopy. Contents of nitrogen, phosphorus, and sulfur in FNPS were found to be 1.53, 2.80, and 0.99 mmol/g, respectively. The phosphorus to nitrogen molar ratio was 1.83. This is very close to the ideal value of 2. The sulfur to nitrogen molar ratio was 0.65. The column-mode test on the Cu(II) uptake from a 0.1 mM Cu(II) aqueous solution revealed that FNPS can take up Cu(II) rapidly even in the extremely high feed flow.
rate range from 1000 to 7000 h⁻¹ in space velocity. The breakthrough capacity of FNPS for Cu(II) is as high as ca. 0.8 mmol/g at the flow rate of 7000 h⁻¹. In addition, it is expected that the FNPS packed column will make it possible to purify huge volumes of waters contaminated with 10⁻⁴ M levels of Zn(II), as long as the concentrations of the co-existing Ca(II) and Mg(II) are nearly equal to those in river waters.

*Keywords:* Bifunctional chelating fiber, Iminodi(methylphosphonate), Sulfonate, Ion exchange, Zinc
1. Introduction

Although chelating resins are useful for selective uptake of heavy metal ions in water, one of their remaining problems is slow kinetics in uptake of metal ions. In column-mode uptake of ions by conventional ion exchange resins, indeed, flow rates of feeds recommended by resin-manufacturers are 20-40 h\(^{-1}\) in space velocity[1-4]. Therefore, two approaches have been proposed to improve kinetic performances of chelating adsorbents. One approach proposed by Alexandratos et al. [5-10] is the introduction of sulfonate as secondary functional group into chelating resins. Because sulfonate is not protonated even in strongly acidic solutions, sulfonate group prevents the decrease in swelling of the resins in acidic solutions caused by protonation of chelating groups, which changes the dissociated chelating groups into the electrically neutral species [3]. In addition, the introduction of sulfonate groups is also effective to depress the Donnan exclusion of metal ions by positively charged chelating groups resulted from the further protonation to the chelating groups in the case of iminodiacetate and aminomethylphosphonate chelating resins. The other approach is the preparation of chelating fibers by the introduction of chelating groups into narrow chemically inert polyolefin fibers [11]. By combining these two approaches mentioned above, we prepared a few bifunctional chelating fibers containing both phosphonate and sulfonate. The introduction of sulfonate groups enhanced both kinetic performances and breakthrough capacities for uptake of heavy metal ions [12].
Recently, we prepared a bifunctional chelating resin containing aminomethylphosphonate and sulfonate from crosslinked poly(ω-bromobutylstyrene) beads of macroreticular type and its metal ion selectivity was studied [2]. As an extension of studies on bifunctional aminomethylphosphonate chelating adsorbents, the present work aimed at the preparation of a bifunctional chelating fiber containing both iminodi(methylphosphonate) and sulfonate with excellent kinetic performances in uptake of heavy metal ions. The objective bifunctional chelating fiber named FNPS (Scheme 1) was derived from a vinylbenzyl chloride grafted polyolefin fiber of the short chopped type. This paper describes the preparation and characterization of FNPS. In addition, its kinetic performances were tested in the column-mode uptake of Cu(II) and Zn(II).

2. Experimental

2.1. Materials

Materials used in the graft polymerization of vinylbenzyl chloride (CMS) were reported in detail elsewhere [11]. The polyolefin fiber used in this work was a short chopped polyethylene-coated polypropylene fiber (0.9 denier, length 3.8 cm), which was provided by Kurashiki Textile Mfg. Co. Osaka, Japan. Hereafter it is abbreviated as PPPEf. The graft polymerization of CMS onto PPPEf
was carried out by nearly the same method described elsewhere [11]. Degree of grafting of CMS (dg%) was designated by the following equation:

\[
\text{dg\%} = 100 \left( \frac{\Delta W}{W_o} \right)
\]

(1)

Here, \( \Delta W \) is a mass increase after graft polymerization and \( W_o \) is the mass of PPPEf before the graft polymerization. In this work, values of dg% is ca. 100, namely, the mass of grafted CMS onto PPPEf is nearly equal to that of PPPEf before the grafting. Reagents were of reagent grade unless otherwise noted.

2.2. Preparation of the bifunctional chelating fiber FNPS

FNPS was prepared according to the synthetic route shown in Scheme 2. This route was established based on a preliminary study on the order of the introduction of two functional groups and sulfonation conditions, such as sulfonation reagents, their concentrations, reaction temperature, and so on. Here, an example of optimized procedures was described to avoid redundant description on the preliminary work. According to Scheme 2, the preparation of FNPS was repeated 6 times to check reproducibility of the syntheses. The dg% values of PPPEf-g-CMS used were 109 and 105 for runs 1-3 and runs 4-6, respectively. Results of elemental analyses are averages of the 6 runs and standard deviation of elemental analyses are also given.
2.2.1. Preparation of FPI by reaction of PPPEf-g-CMS with potassium phthalimide

PPPEf-g-CMS (1.0 g, dg% = 105, C 78.20%, H 9.92%), potassium phthalimide (1.9 g) and N,N-dimethylformamide (50 mL) were taken into a pressure-resistant glass tube. After sealing the tube tightly, the resulting mixture was heated at 80 °C for 2 h on an oil bath. During heating, the tube was occasionally shaken. The fiber was filtered off and successively washed with acetone and water. After air-drying, the resulting fiber named FPI was dried in a vacuum oven at 40 °C for 24 h. CHN analysis: C 79.18 ± 0.62%, H 8.46 ± 0.13%, N 3.10 ± 0.06%. Fourier transform infrared (FT-IR) spectrum (KBr): 1772, 1714 cm⁻¹ (phthalimide group, ν(C=O)).

2.2.2. Preparation of FPIS by sulfonation of FPI with sulfuric acid

FPI (1.3 g) was reacted with sulfuric acid (95 wt%, 40 mL) in a 100 mL Erlenmeyer flask at 40 °C for 6 h. The resulting fiber was washed with ethanol, water, and acetone successively. After air-drying, it was dried in a vacuum oven at 40 °C for 24 h. CHN analysis: C 69.65 ± 0.74%, H 8.17 ± 0.21%, N 2.35 ± 0.12%. FT-IR spectrum (KBr): 1169, 1020 cm⁻¹ (SO₃H), 1771, 1710 cm⁻¹ (phthalimide group, ν(C=O)).

2.2.3. Preparation of FNS by hydrolysis of FPIS with hydrazine hydrate
FPIS (1.3 g) and an ethanol solution of hydrazine hydrate (5wt\%, 50 mL) were taken into a pressure-resistant glass tube. After sealing the tube tightly, the tube was allowed to stand at 80 °C for 2 h on an oil bath under occasional shaking the tube. Then, the resulting fiber was washed with ethanol, water, 0.1 M HCl, 1 M NaOH and water successively, and then air-dried. Finally, the fiber was dried in a vacuum oven at 40 °C for 24 h. CHN analysis: C 67.28 ± 1.02\%, H 9.51 ± 0.18\%, N 3.17 ± 0.18\%. S analysis: 4.68 ± 0.29\% for runs 1, 2, and 3. FT-IR spectrum (KBr): 3432 cm⁻¹ v(N-H), 1178, 1021 cm⁻¹ (SO₃H).

2.2.4. Preparation of FNPS by the Mannich condensation of FNS

Primary amino groups in FNS were converted into iminodi(methylphosphonate) by the Mannich condensation reaction. FNS (0.9 g), phosphorous acid, paraformaldehyde, and 6 M HCl (50 mL) were taken into a pressure-resistant glass tube and the tube was sealed tightly; here, amounts of phosphorous acid and paraformaldehyde were 60 and 30 molar times the molar nitrogen content in FNS. The resulting mixture was heated at 100 °C on an oil bath. During heating, the tube was occasionally shaken. After cooling the reaction mixture, the functionalized fiber was filtered off and it was packed into a glass column. Then, 1 M HCl (300 mL) was fed to the column for washing the fiber, and finally the fiber was equilibrated with a dilute HCl of pH 2.0. After air-drying the fiber, it was dried in a vacuum oven at 40 °C for 24 h. CHN analysis: C 53.32 ± 1.65\%, H 8.14 ± 0.18\%, N
2.14 ± 0.11%. Chemical analysis of S and P: S 3.17±0.10%, P 8.67±0.27%. FT-IR spectrum(KBr): 3400 cm⁻¹, ν(N-H), 2560-2700 cm⁻¹ (O=P-OH), 1180-1150 cm⁻¹, 1083 cm⁻¹ ν(PO, P=O), 1175, 1020 cm⁻¹ (SO₃H).

2.3. Column-mode adsorption and elution operations

2.3.1. Column preparation

FNPS (0.40 g in dry state) was immersed in water for swelling. FNPS swollen with water was packed into a polyethylene column (i.d. 1.3 cm). The column had two polyethylene filters; one was placed at the bottom of the column and the other was at the top of the fiber bed to fix the fiber bed volume at constant.

2.3.2. Adsorption and elution operations

Feeds in the adsorption operation were aqueous solutions of metal ions. The feeds were supplied to the column by changing the flow rate. Compositions and flow rates of the feeds will be given in later sections in detail with results. After the supply of the feeds, the column was washed with 10-20 bed volumes (BV) of water. Metal ions adsorbed on the columns were eluted with 1 M HCl. After the elution operation, the column was washed with water and equilibrated with a dilute HCl of pH
2.0 for the next adsorption operation. Flow rates of the eluents, water, and the dilute HCl of pH 2.0 were 5 h⁻¹ in space velocity.

All column effluents including washings were collected on a fraction collector unless otherwise specified. When concentrations of the target ion in feeds were equal to or less than 1 mM, column effluents in the adsorption operations were taken into a series of 500 mL volumetric flasks. The total uptake (TU) of the target ion in the adsorption operations was calculated from the following equation:

\[
TU(\text{mmol/g}) = \left( C_f V_f - \sum_{i=1}^{n} C_i V_i \right) / m \quad (2)
\]

where \( C_f \) and \( V_f \) are the concentrations of the target ion in the feed and the volume of the feed supplied to the column, respectively, and where \( C_i, V_i, \) and \( n \) are the target ion concentration in the i-th fraction, the volume of the i-th fraction, and the number of the last fraction in the adsorption operation including column washing just after the end of the feed supply. The breakthrough capacity (BC) of FNPS for the target ion was calculated from the following equation:

\[
BC(\text{mmol/g}) = \left( C_f V_b - \sum_{i=1}^{n'} C_i V_i \right) / m \quad (3)
\]

Here, \( V_b \) is the volume of the feed up to the breakthrough point and \( n' \) is the fraction number at the breakthrough point. In this work, the breakthrough points of target ions were designated as the volume of the feed corresponding to \( C_i / C_f = 0.05 \). The amount of metal ion eluted (AME) was calculated from the equation (4).
\[ AME(\text{mmol/g}) = \left(1/m\right) \sum_{j=1}^{n} C_j V_j \]  \hspace{1cm} (4)

Here, \( C_j \), \( V_j \) and \( n' \) are the concentration of the target ion in the j-th fraction, the volume of the j-th fraction, and the number of the last fraction in the elution operations, respectively. Most adsorption-elution-regeneration operations for a given condition were duplicated to check the reproducibility.

2.4. Measurements

Sulfur in fiber samples was measured by means of a flask combustion method, in which sulfate resulting from combustion of fiber samples was analyzed with a Jasco ion chromatography system (Jasco Co., Tokyo, Japan). Phosphorus content of fiber samples was measured by combination of complete digestion of fiber samples with nitric and perchloric acids at elevated temperature and spectrophotometric determination of resulting phosphoric acid [13]. The ICP-AES instrument used in the determination of metal ions was a CID Plasma Photoemission Spectrophotometer IRIS (Nippon Jarrell Ash Co., Kyoto, Japan). Metal ion standard solutions for the instrument calibration were purchased from Wako Pure Chemical Industries Ltd., Osaka, Japan.

3. Results and discussion
3.1. Characterization of intermediates and FNPS

FT-IR spectrum of PPPEf-g-CMS exhibits a sharp band at 1265 cm\(^{-1}\), which is characteristic of chloromethyl groups. This band was not observed in the FT-IR spectrum of FPI but bands were observed at 1772 and 1714 cm\(^{-1}\), which can be assigned to stretching bands of carbonyl groups in phthalimide moieties fixed to the fiber. The yield was 92% under the assumption that weight increase after the graft polymerization comes from the grafted CMS only. Hereafter, we would like to point out that it is difficult to compare the analytical value of each element with calculated one, because the manufacturer of PPPEf did not disclose its detailed composition, such as the polyethylene to polypropylene weight ratio. Hereafter, therefore, we mainly refer to contents of nitrogen, sulfur and phosphorus.

Sulfonation of FPI was carried out using 95% sulfuric acid at a mild temperature of 40 °C based on the preliminary study on sulfonation. In the FT-IR spectrum of the resulting FPIS, bands of sulfonate groups were observed at 1169 and 1020 cm\(^{-1}\) in addition to bands of carbonyl groups at 1771 and 1710 cm\(^{-1}\). Next the hydrolysis of phthalimide moieties in FPIS was carried out by heating FPIS in an ethanol solution of hydrazine hydrate, resulting in FNS having primary amino groups. In the FT-IR spectrum of FNS, the bands of carbonyl groups were not observed but the band of primary amino groups was observed around 3430 cm\(^{-1}\). Bands of sulfonate groups were observed at
1178 and 1021 cm\(^{-1}\). The nitrogen and sulfur contents in FNS were 2.26±0.13 and 1.46±0.09 mmol/g, respectively. The sulfur to nitrogen molar ratio is 0.646; namely, the molar content of sulfonate is two third that of amino groups. This molar ratio is pertinent because the selectivity of the bifunctional resin is governed by molar fractions of the two functional groups [14].

Application of the Mannich condensation reaction to FNS gave the objective fiber FNPS. Fig.1 shows the FT-IR spectrum of FNPS in its hydrogen ion form. FNPS has sulfonate and iminodi(methylphosphonate) groups. Unfortunately, sulfonate and phosphonate groups absorb at 1000-1200 cm\(^{-1}\). By comparing the FT-IR spectrum of FNS with that of FNPS and referring to the work reported by Matveeva et al. [15], the bands at 1180-1150 and 1083 cm\(^{-1}\) were assigned to stretching vibrations of PO\(_2\). Table 1 shows contents of nitrogen, phosphorus, sulfur, and acid capacity of FNPS. The phosphorus to nitrogen molar ratio is 1.8, which is higher than 1.4 for the corresponding bifunctional chelating resin derived from the macroreticular poly(\(\omega\)-bromobutylstyrene) crosslinked with 10 mol% divinylbenzene [2]. This means that the Mannich condensation reaction proceeded more ideally in the case of the fiber than the case of highly crosslinked macroreticular resin because the grafted polymer chains in PPPEf-g-CMS are not crosslinked with any divinyl monomer. Probably, the steric hindrance for the functionalization reactions in the grafted fiber is lower than that in the crosslinked resin. As long as FNSP has only sulfonate and iminodi(methylphosphonate) groups, its acid capacity is equal to 2m\(_{p}^+\) m, meq/g; here
mp and ms are molar contents of phosphorus and sulfur, respectively. The observed acid capacity of 6.0 meq/g was less than the calculated value of 6.6 meq/g. Since pKa4 of CH3-N(CH2PO3H2)2 is 12.1 [16,17], it is estimated that pKa5 of FNPS is greater than 12. Then, it is plausible that the acid capacity of FNPS is less than the value calculated from 2mp+ms. The sulfur to nitrogen molar ratio of FNPS is 0.647, which is very close to that of the precursor FNS. In addition, the phosphorus to nitrogen molar ratio is 1.83, which is also very close to the ideal value of 2. From analytical and FT-IR spectral data, it can be concluded that FNPS has a statistical structure of Mat·0.65(-SO3H)·0.83(-N(CH2PO3H2)2)0.17(-NCH2PO3H2); here Mat is the polymer matrix except for the functional groups (-SO3H, -NCH2PO3H2, and -N(CH2PO3H2)2).

3.2. Column-mode uptake of Cu(II)

Cu(II) forms stable complexes with most organic ligands containing both nitrogen and oxygen donors. Then, we are interested in Cu(II) to test a newly prepared chelating resins and fibers [11,12]. Recently, we reported that the phosphonate fiber FCP can take up Cu(II) up to the feed flow rate of 1000 h⁻¹ in space velocity and the introduction of sulfonate as the second functional group into the phosphonate fiber enhances greatly the kinetic performances for column-mode uptake of Cu(II) even at high flow rate of feeds [12]. Therefore, it is expected that the FNPS packed column will be able
to take up Cu(II) from a feed at much higher flow rates. Then, at first, breakthrough profiles of Cu(II) were evaluated by feeding 6.00 L of 0.1 mM aqueous Cu(NO₃)₂ solution to the column at flow rates of 1000, 3000, 5000 and 7000 h⁻¹ in space velocity (SV). Fig. 2 shows examples of breakthrough profiles of Cu(II) and Table 2 lists numerical data of all runs. Because the purpose is to evaluate the breakthrough capacity, the feed supply was not continued up to C/C₀ = 1.

Judging from Fig. 2 and Table 2, the breakthrough point and the breakthrough capacity slightly decreased with an increase in the feed flow rate. Even at the highest flow of 7000 h⁻¹, the breakthrough capacity is as high as ca. 0.80 mmol/g-fiber, which corresponds to two thirds of the breakthrough capacity at the flow rate of 1000 h⁻¹ (ca.1.2 mmol/g-fiber). Total uptake of Cu(II) also slightly decreases with an increase in the feed flow rate but its decrease is not so marked compared with that of the breakthrough capacity. The adsorbed Cu(II) on FNPS was able to be quantitatively eluted with a 1 M HCl. During the elution operation of Cu(II), FNPS was regenerated into the hydrogen ion form and then it was equilibrated with a dilute HCl of pH 2.0 for the next adsorption operation. The column was able to be used repeatedly, as shown in Table 2.

Although the flow rate of 7000 h⁻¹ is at least 175 times faster than the recommended flow rate of 20-40 h⁻¹ for granular ion exchange resin packed columns [1-4]. In addition, the feed can be supplied without a marked increase in the column pressure loss using a peristaltic pump. However, the flow rate above 7000 h⁻¹ was difficult to achieve because of the column pressure loss. At the feed flow
rate of 7000 h\(^{-1}\), the linear velocity of the feed in the column was 9.7 m h\(^{-1}\) (2.69 cm s\(^{-1}\)) and the average residence time in the fiber bed was only 0.51 s.

In addition to the excellent kinetic performances, FNPS has a more advantage in the column-mode use; this is a low pressure loss of the FNPS packed column at high flow rates. As reported in a previous paper, the monofunctional iminodiacetate chelating fiber (FIDA) derived from PPPE\(_{f-g}\)-CMS [11] markedly changed its swelling volumes with pH; the swelling volume of FIDA increases with an increase in pH, because the degree of dissociation of iminodiacetic acid markedly increases with an increase in pH. The high swelling increases the column pressure loss, so that the tolerable flow rates of the feed decreases with an increase in pH. Indeed, the highest flow rate for uptake of Cu(II) by FIDA was 600 h\(^{-1}\) at pH 2.0, but that at pH 4.6 decreased down to 300 h\(^{-1}\)[11]. Sulfonate in the bifunctional fibers dissociates completely even in strongly acidic conditions and then it relaxes the drastic swelling volume change with pH. Then, it became possible to supply the feed up to the flow rate of 7000 h\(^{-1}\) in space velocity.

3.3. Use of FNPS in the rapid column-mode removal of Zn(II) from water

3.3.1. Removal of Zn(II) from 10 mM Zn(NO\(_3\))\(_2\) solutions

In 2006, Japanese Government tightened the effluent regulation of Zn(II) from 5 mg/L to 2 mg/L
from viewpoint of the aquatic life conservation. This led us to the study on the column-mode removal of Zn(II) by FNPS under various conditions. Our recent study clarified that Zn(II) is hardly distributed into the monofunctional aminomethylphosphonate resin RC4NP from strongly acidic solutions of pH 2.0. Even at pH 2.0, on the other hand, Zn(II) is quantitatively distributed into the bifunctional chelating resin containing both aminomethylphosphonate and sulfonate RC4NPS [2]. This predicts that FNPS will successfully take up Zn(II) from strongly acidic solutions of pH 2.0. Then, the column-mode uptake of Zn(II) was carried out by feeding a 10 mM Zn(NO$_3$)$_2$ solution of pH 2.0 to the FNPS packed column at flow rates of 50, 100, 200, and 1000 h$^{-1}$. Fig. 3 shows the breakthrough profiles of Zn(II) and Table 3 summarizes detailed experimental conditions and numerical results. Fig. 4 shows an example of the elution of the Zn(II) adsorbed on FNPS with 1 M HCl. Within 6 bed volumes of 1 M HCl, Zn(II) was quantitatively eluted.

From the strongly acidic solution of pH 2.0, FNPS took up Zn(II) as expected. With an increase in the flow rate of feed from 50 to 1000 h$^{-1}$, the decrease in the breakthrough capacity was only 18%. Because the values of C/C$_0$ are nearly equal to unity above 50 bed volumes of the feed as shown in Fig. 3, total uptake of Zn(II) is nearly equal to the equilibrium capacity at pH 2.0. Then, the total capacity is essentially independent of the feed flow rate as judged from Table 3.

Conditional stability constants of metal complexes with ligands containing nitrogen donors increase with an increase in pH. Then, Zn(II) uptake from a 10 mM Zn(II) solution of pH 5.4 was
also examined at two feed flow rates of 1000 and 2000 h\(^{-1}\). The results are also given in Table 3. In the case of the flow rate 1000 h\(^{-1}\), the breakthrough capacity for the feed of pH 5.4 was 0.90 mmol/g, which is greater than that for the feed of pH 2.0 by 28%. With increasing the flow rate of the feed from 1000 to 2000 h\(^{-1}\), the decrease in the breakthrough capacity was small (ca. 0.1 mmol/g).

In the case of Zn(II) uptake from the solutions of pH 5.4, the value of C/Co approached to unity at the 97 bed volumes of the feed (Entry Z9 in Table 3). Then the total uptake in Entries Z8, Z10 and Z11 is far from the equilibrium capacity, because the volume of the feed supplied to the column was 49.7-64.2 bed. This is the reason why the total uptake in Entries Z8-Z9 is changed greatly. The Zn(II) uptake after the breakthrough points does not have practical meaning from the viewpoint of the purification of water contaminated with Zn(II). Then, the feed was not supplied up to the value of C/Co = 1. However, data given in Table 3 clearly suggest that the repeated use of FNPS is possible.

**3.3.2. Dependence of breakthrough capacity on the Zn(II) concentration in feeds**

In order to clarify the effect of the Zn(II) concentration of the feeds on the breakthrough capacity of FNPS for Zn(II), the adsorption operation were carried out using 1 mM and 0.1 mM Zn(NO\(_3\))\(_2\) solutions as feed. Because the main purpose here is the determination of the breakthrough capacity, the feeds were not always supplied to the column up to C/Co = 1. The results are summarized in
Table 4. Interestingly, the breakthrough capacity increases with a decrease in the Zn(II) concentration in the feeds. This phenomenon is probably ascribable to an increase in the supplied feed volume with a decrease in the Zn(II) concentration of the feeds. The lower the Zn(II) concentration of the feeds, the larger the supplied feed volume up to the breakthrough point. Since the conditioned FNPS was initially in the hydrogen ion form, the hydrogen ion as counter ion of chelating groups was partially neutralized with a trace amount of HCO$_3^-$ contained in the feeds. The amount of neutralized chelating groups increases with an increase in the supplied feed volume. The supplied feed volume increases with a decrease in the Zn(II) concentration of the feed as listed in the third column of Table 4. Therefore, it is observed that the breakthrough capacity increases with a decrease in the Zn(II) concentration of the feed. As described here, FNPS can take up Zn(II) from $10^{-4}$ M (6.5 mg/L) level Zn(II) solutions at the high flow rate of 1000 h$^{-1}$.

3.3.3. Effect of Ca(II) and Mg(II) on uptake of Zn(II)

Since possible interferents in the Zn(II) removal from river water are Ca(II) and Mg(II), their influence on the removal of Zn(II) was studied using binary solutions containing Zn(II) and Ca(II) (or Mg(II)) as feed. Average concentrations of Ca(II) and Mg(II) in river waters in Japan are 8.8 mg/L (0.220 mM) and 1.9 mg/L (0.0782 mM), respectively [18]. Referring to these data, the binary solutions as the feed were prepared as listed in the second column of Table 5.
Fig. 5 shows breakthrough profiles of Zn(II) and Ca(II) in the competitive uptake of both metal ions, and the breakthrough profile of Zn(II) in the non-competitive uptake is also shown for comparison. The average of breakthrough capacities for Zn(II) is 0.66 and 1.28 mmol/g for the competitive and non-competitive cases, respectively. The average Ca(II) to Zn(II) molar ratio in the feed is 2.34. Despite the presence of excess Ca(II), Ca(II) leaked earlier than Zn(II) as shown in Fig. 5. In addition, the C/C₀ values for Ca(II) exceeded unity after 1000 bed volumes of the feed because of the substitution elution of the Ca(II) adsorbed at the beginning stage of the feed supply by more preferred Zn(II). Even in the presence of excess Ca(II), ca. 1000 bed volumes of the water containing 8 mg of Zn(II)/L was purified down to the concentration less than 0.4 mg of Zn(II)/L for only 1 h.

Fig. 6 shows the breakthrough profiles of Zn(II) and Mg(II) during the competitive uptake of Zn(II) and Mg(II) from the feed, in which the Mg(II) to Zn(II) molar ratio is 1.2. The breakthrough capacity of Zn(II) is 0.83 mmol/g. This is 65% of the breakthrough capacity without any interferent. Similar to the competitive uptake of Ca(II) and Zn(II), the C/C₀ value for Mg(II) exceeded unity above 1500 bed volumes of the feed, indicating that FNPS prefers Zn(II) to Mg(II). In the presence of slight excess Mg(II), 1500 bed volumes of water containing 7 mg of Zn(II)/L can be purified to the concentration less than 0.3 mg of Zn(II) /L for only 1.5 h.

As conclusion, it is expected that FNPS will make it possible to purify huge volumes of waters
contaminated with $10^{-4}$ M levels of Zn(II), as long as the concentrations of the co-existing Ca(II) and Mg(II) are nearly equal to those in river waters in Japan.

4. Conclusions

The bifunctional chelating fiber named FNPS was derived from a vinylbenzyl chloride grafted polyethylene-coated polypropylene fiber (PPPEf-g-CMS). FNPS has sulfonate groups as secondary functional group in addition to the primary iminodi(methylphosphonate) chelating groups. First, PPPEf-g-CMS was reacted with potassium phthalimide to substitute chlorine atoms in PPPEf-g-CMS with phthalimide moiety. Sulfonate groups were introduced into the phenyl groups of benzyl moieties on the grafted polymer chains by the reaction with 95% sulfuric acid, and then phthalimide moieties were hydrolyzed with ethanol solution of hydrazine hydrate to yield the primary amino groups at the end of benzyl moieties on the grafted chains. Then these primary amino groups were converted into iminodi(methylphosphonate) groups by Mannich condensation reaction using large excess phosphorous acid, paraformaldehyde, and 6 M hydrochloric acid under refluxed conditions for 6 h, resulting in the objective FNPS. The sulfonate and iminodi(methylphosphonate) groups in FNPS were identified by measurement of its FT-IR spectrum. Contents of nitrogen, phosphorus, and sulfur in FNPS were 1.53, 2.80, and 0.99 mmol/g, respectively. Therefore, the
phosphorus to nitrogen molar ratio was 1.83. This is close to the ideal value of 2. The sulfur to nitrogen molar ratio was 0.65.

The column-mode test on the Cu(II) uptake from 0.1 mM Cu(II) solution revealed that FNPS can take up Cu(II) rapidly even at the extremely high feed flow rate of 1000-7000 h\(^{-1}\) in space velocity and the breakthrough capacity of FNPS for Cu(II) is as high as ca. 0.80 mmol/g at the flow rate of 7000 h\(^{-1}\). In addition, it is expected that the FNPS column will be suitable for the rapid purification of huge volumes of freshwaters contaminated with \(10^4\) M levels of Zn(II), as long as the concentrations of the co-existing Ca(II) and Mg(II) are nearly equal to those in river waters in Japan.

**Acknowledgement**

We are grateful to the Steel Industry Foundation for the Achievement of Environmental Protection Technology of Japan for the financial support for this work.

**References**


Scheme Captions

Scheme 1. Structure of FNPS.

Scheme 2. Synthetic route of chelating fiber FNPS.
Figure Captions

Fig. 1. FT-IR spectrum of FNPS in the hydrogen ion form.

Fig. 2. Effect of the flow rate of the feed on column-mode uptake of Cu(II) by FNPS.

Flow rate of the feed in space velocity (h⁻¹): ○ 1000(C2), △ 3000(C4), □ 5000(C6), ● 7000(C8). Here, C2, C4, C6 and C8 in parentheses are Entries in Table 2. For detailed conditions, refer to Table 2.

Column: FNPS 0.40 g in dry state, 1.84 mL in wet state.

Fig. 3. Breakthrough profiles of Zn(II) in column-mode uptake by FNPS from 10 mM Zn(II)

solution of pH 2.0.

Flow rate of feed in space velocity (h⁻¹): ▲ 50 (Z1), ● 100 (Z2), △ 200(Z4), and ○ 1000 (Z6).

Here, Z1, Z2, Z4 and Z6 in parentheses are Entries in Table 3. For detailed conditions, refer to Table 3. Column: 0.40 g in dry state, 2.1 mL in wet state.

Fig. 4. Elution of Zn(II) adsorbed on FNPS with 1 M HCl.

Flow rate of the eluent: 5 h⁻¹ in space velocity.

For detailed conditions of the adsorption operation, refer to Entry Z2 in Table 3.
Fig. 5. Breakthrough profiles of Zn(II) and Ca(II) in competitive uptake of Zn(II) and Ca(II).

Run1 (Entry Z16) ○Zn(II) △Ca(II), Run2 (Entry Z17) ●Zn(II) ▲Ca(II), □Zn(II) only (Entry Z13).

For detailed conditions, refer to Entries Z16, 17 and Z13 in Table 5. Column: FNPS 0.40 g in dry state, 2.1 mL in wet state.

Fig. 6. Breakthrough profiles of Zn(II) and Mg(II) in competitive uptake of Zn(II) and Mg(II).

Run1 (Entry Z18) ○Zn(II) ▽Mg(II), Run2 (Entry Z19) ●Zn(II) ▼Mg(II).

For detailed conditions, refer to Entries Z18, Z19 in Table 5.

Column: FNPS 0.40 g in dry state, 2.1 mL in wet state.
Table Captions

Table 1

Contents of key elements and acid capacity of FNPS.

Table 2

The effect of flow rate on uptake of Cu(II) by FNPS.

Table 3

Flow rate dependence of Zn(II) uptake by FNPS packed column from 10 mM Zn(NO$_3$)$_3$ of pH 2 or pH 5.4.

Table 4

Dependence of breakthrough capacity for Zn(II) on concentration of Zn(II) in feeds.

Table 5

Results on competitive uptake of Zn(II) with Ca(II) or Mg(II).