

Preparation and Characterization of Bifunctional Chelating Fiber Having Aminomethylphosphonate and Sulfonate Groups

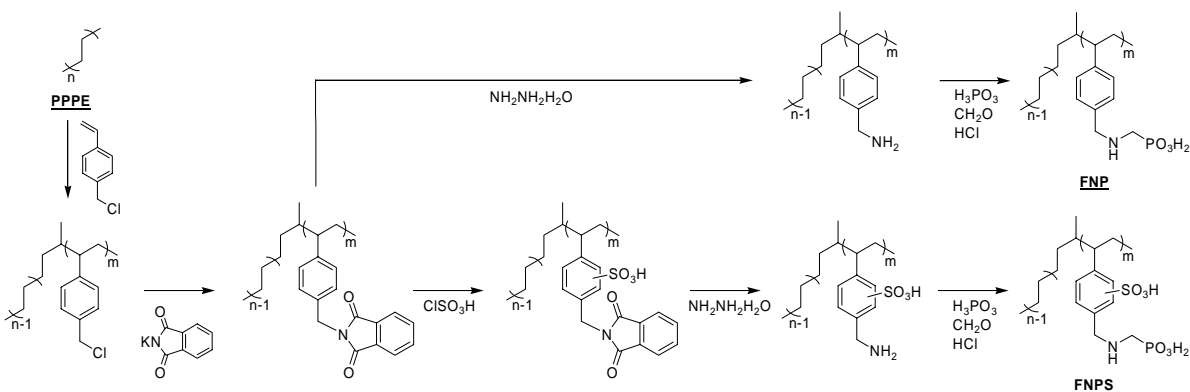
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Although aminomethylphosphonate resins have been used in the removal of heavy metal ions from various wastewaters, one of their serious disadvantages is slow kinetics in the adsorption of heavy metal ions. For instance, the recommended flow rate of feeds is less than 30 h^{-1} in space velocity (SV) in the case of one of typical aminomethylphosphonate resins Duolite C-467 packed column [1]. Alexandratos et al. have proposed bifunctional chelating resins having sulfonate groups as the secondary functional group in addition to the primary chelating groups; here sulfonate groups assist uptake of metal ions by the primary chelating groups through the high swelling caused by sulfonate groups [2]. Recently, we have been studying bifunctional chelating fibers to improve kinetic aspects of chelating exchangers [3]. In this work, a bifunctional aminomethylphosphonate/sulfonate fiber was developed and its properties were compared with those of the corresponding monofunctional fiber.

Fibers adopted as trunk polymer were polyethylene coated polypropylene fiber (PPPE-f, 0.9 denier) and its non-woven cloth (PPPE-c, 1.5 denier). Chloromethylstyrene (CMS) was grafted onto each trunk polymer as described [4], and CMS contents in both resulting grafted fibers CMS-g-PPPE-c and CMS-g-PPPE-f were about 1 g per g of trunk polymer. Both CMS-g-PPPE-c and CMS-g-PPPE-f were functionalized according to a series of reactions shown in Scheme 1, resulting in the bifunctional fibers FNPS-c and FNPS-f, respectively. For the sake of comparison, the corresponding monofunctional fibers FNP-c and FNP-f were also prepared. After each functionalized fiber was equilibrated with dilute hydrochloric acid of pH 2, it was air-dried. Finally it was dried in vacuum at $40 \text{ }^\circ\text{C}$ for more than 24 h. The four objective fibers thus conditioned were characterized by FT-IR spectroscopy and elementary analysis. In the further study, the cloth type fibers (FNPS-c and FNP-c) were used in the batch mode selectivity study, and the filamentary ones (FNPS-f and FNS-f) in the column mode study.



Scheme 1 Preparation routes of monofunctional and bifunctional aminomethylphosphonate fibers

Table 1 summarizes chemical properties of four kinds of the functionalized fibers. Both monofunctional fibers FNP-c and FNP-f have nearly equal phosphorus and nitrogen contents, and their

capacities are slightly greater than $2m_p$; here m_p means phosphorous content in mmol/g. This may mean that some functional groups exist as the form of $[-NH_2^+-CH_2-P(O)(OH)_2][Cl^-]$. The sulfur content of FNPS-f is much greater than that of

Table 1 Properties of chelating fibers

Chelating fiber	P content (mmol/g)	N content (mmol/g)	S content (mmol/g)	Molar ratio of P to N	Acid capacity (meq/g)
FNP-c	2.3	1.8	-	1.3	5.0
FNP-f	2.2	2.1	-	1.1	5.6
FNPS-c	1.6	1.6	0.7	1.0	4.1
FNPS-f	2.3	1.8	3.1	1.3	5.3

FNPS-c. This came from the difference in the concentration of chlorosulfonic acid used in the sulfonation step between FNPS-f and FNPS-c. In the preparation of FNPS-c and FNPS-f, 5 % and 10 % chlorosulfonic acid in dichloromethane were used, respectively. The higher concentration of chlorosulfonic acid resulted in the higher sulfur content. The acid capacity of FNPS-c is nearly equal to $2m_p + m_s$ as expected, but that of FNPS-f is much less than the expected value. Here, m_s is sulfur content in mmol/g. At the present, it is not clear why FNPS-f gives the acid capacity less than the estimated one from elementary analysis.

The metal ion selectivity of both FNP-c and FNPS-c were evaluated by batchwise measurement of pH dependency of the distribution of Ca(II), Cd(II), Ni(II), Pb(II), and Zn(II) from nitric acid media into respective fibers. The results led to the selectivity sequence of Pb(II) > Cd(II) > Ca(II) ~ Zn(II) > Ni(II) for both fibers, indicating the highest selectivity toward Pb(II) as in the case of a typical commercially available aminomethylphosphonate resin Duolite C-467, which prefers Pb(II) to other common divalent metal ions [1].

In the column mode study, Cu(II) adsorption abilities of FNP-f and FNPS-f were evaluated; here, a solution containing 10 mM $Cu(NO_3)_2$ was supplied to respective columns packed with FNP-f and FNPS-f. Figures 1 and 2 show the results; in the case of the monofunctional fiber FNP-f, Cu(II) leaked from the column just after the start of the feed supply, indicating that FNP-f cannot efficiently take up Cu(II) even at a flow rate of $50 h^{-1}$ in space velocity, whereas FNPS-f gives a clear breakthrough points of ca. 20 mL/mL of fiber (0.70 mmol/g of dried fiber) at the flow rate of $50 h^{-1}$. Although the breakthrough points of Cu(II) decreases with an increase in the flow rate, it can be concluded that the bifunctional FNPS-f exhibits much faster kinetics in the adsorption of Cu(II) than the monofunctional FNP-f and commercially available monofunctional aminomethylphosphonate resins as well.

References

- [1] H. Simizu, (Ed.), "Kyucyaku Gijyutsu Handobukku (in Japanese, Handbook of Adsorption Technology)", NTS Pub. Co., Tokyo, 1993, p. 391.
- [2] S. D. Alexandratos, S. Natesan, *Eur. Polym. J.*, **35**, 431-436(1999).
- [3] A. Jyo, K. Okada, M. Nakao, T. Sugo, M. Tamada, A. Katakai, *J. Ion Exchange*, **14**(Supplement), 69-72(2003).
- [4] A. Jyo, S. Aoki, T. Kishita, K. Yamabe, M. Tamada, T. Sugo, *Anal. Sci.*, **17**(Supplement), i201-i204(2001).

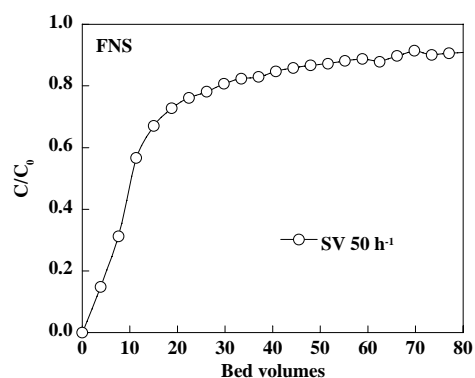


Fig. 1 Breakthrough profile of Cu(II)
Column: 1.3 mL of FNP-f (H^+ form, 0.4 g in dry state),
Feed: 0.01 M Cu(II)

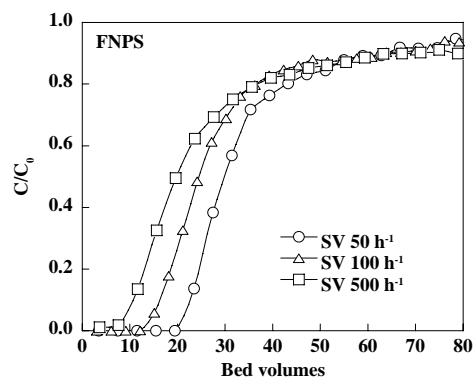


Fig. 2 Effect of the flow rate on the adsorption of Cu(II)
Column: 1.4 mL of FNPS-f (H^+ form, 0.4 g in dry state),
Feed: 0.01 M Cu(II)