Properties of Bifunctional Phosphonate Fibers Derived from Chloromethylstyrene Grated Polyolefine Fibers

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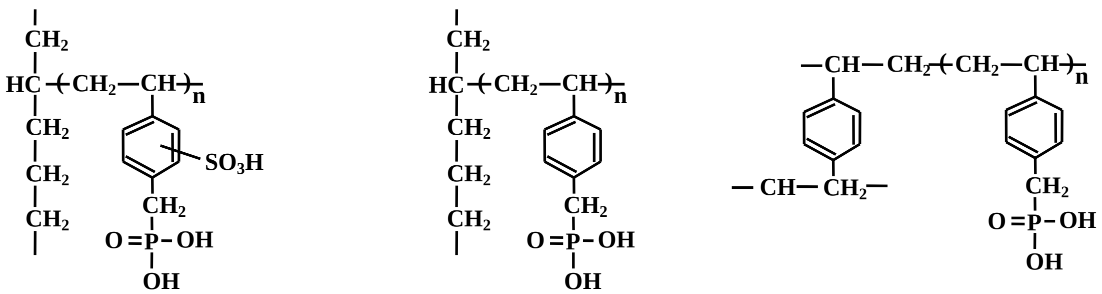
Since phosphonates exist as electrically neutral protonated species in the strongly acidic range below pH 2, phosphonate resins do not highly swell and cannot efficiently take up metal ions from such strongly acidic solutions. In order to resolve this problem, Alexandratos et al. have proposed phosphonate/sulfonate bifunctional resins [1], in which sulfonate groups enhance swelling of resins even in strongly acidic solutions, leading to their efficient uptake of metal ions. Recently, we have reported that the phosphonate/sulfonate bifunctional fiber derived from vinylbiphenyl grafted polyolefine fiber can take up rapidly Fe(III) even at a surprisingly high flow rate of 1000 h^{-1} in space velocity [2]. However, vinylbiphenyl is a novel vinyl monomer which is not available in industrial scale yet. In this work, therefore, a phosphonate/sulfonate bifunctional fiber named FCPS was prepared from chloromethylstyrene grafted polyolefine fiber, and its metal ion adsorption ability was studied mainly by a columnar method. For the sake of comparison, the monofunctional phosphonate fiber FCP and resin RCSP were also used.



FCPS FCP RCSP

The polyolefine fiber used was a polyethylene coated polypropylene fiber (0.9 denier) named PPPE-f. The graft polymerization of chloromethylstyrene (CMS) onto PPPE-f was conducted by an electron beam pre-irradiation induced liquid graft polymerization method as reported elsewhere [3]. Amount of the grafted CMS onto PPPE-f was 1.39g per g of PPPE-f. First, the functionalization of the CMS grafted PPPE-f was conducted according to the reported method [1]; namely, introduction of phosphonate ester on to CMS grafted fiber by Arbusov reaction, sulfonation with chlorosulfonic acid, and acid hydrolysis of phosphonate ester in refluxed 12 M hydrochloric acid, in successive. In this method, however, sulfonation process markedly reduced phosphorus and sulfur contents of the resulted fiber. Consequently, the order of the functionalization reactions was changed to the following order: Arbusov reaction, acid hydrolysis, and sulfonation. This modification led to satisfactory results. Table 1 shows properties of the resulting phosphonate/sulfonate bifunctional fiber FCPS with those of the monofunctional phosphonate fiber (FCP) and resin (RCSP). Phosphorus content of FCP was somewhat lower than that of FCSP. This is due to the fact that FCP used here was prepared before optimization of reaction conditions. All fiber and resin were used in the hydrogen ion form.

Table 1 Properties of FCSP, FCP, and RCSP

Fiber	Phosphorus content (mmol/g)	Sulfur content (mmol/g)	Acid capacity (meq/g)
FCPS	2.2	1.2	6.1
FCP	1.8	-	3.6
RCSP	4.4	-	7.1

Into a polypropylene column (i.d. 1.3 cm), wet FCPS or FCPS (0.4 g as dry state of each) was packed. The fiber bed volume in each column was 1.5 mL. In the case of RCSP, its wet sample (0.49g as dry state) was packed into a glass column (i.d. 0.7 cm) and the bed volume was also 1.5 mL. To respective columns, feeds containing mM levels of $Cu(NO_3)_2$ were supplied. Flow rates of the feeds were 10 - 1000 h^{-1} for both fiber columns and 10 - 500 h^{-1} for the resin column. After washing the column with water, adsorbed Cu(II) was eluted with 1 M HNO_3. All effluents were collected on a fraction collector. The concentration of Cu(II) in each fraction was measured by means of ICP-AES.

Figure 1 illustratively shows breakthrough profiles of Cu(II). In uptake of Cu(II) by the resin RCSP, breakthrough points are highly dependent on flow rates of the feed as shown in Fig. 1. Although RCSP gives a breakthrough capacity of ca. 1 mmol/g at flow rate of 10 h^{-1}, it does only ca. 0.1 mmol/g at the flow rate of 500 h^{-1}. On the other hand, breakthrough capacities of FCP and FCPS were not markedly dependent on flow rates. Indeed, they give the breakthrough capacities of ca. 0.3 and ca. 0.8 mmol/g for Cu(II) even at the highest flow rate of 1000 h^{-1}, respectively, as judged from Fig. 1. The resin RCSP has a high phosphonate content of 4.4 mmol/g but cannot rapidly take up Cu(II) at the high flow rate of more than 500 h^{-1}, and the most suitable flow rate for RCSP is 10 h^{-1}. Opposed to the granular RCSP, both fibers FCP and FCPS exhibit extremely rapid adsorption rates. In particular, only the bifunctional fiber FCPS can give large breakthrough capacities of ca. 0.8 mmol/g even at the high flow rate of 1000 h^{-1}.

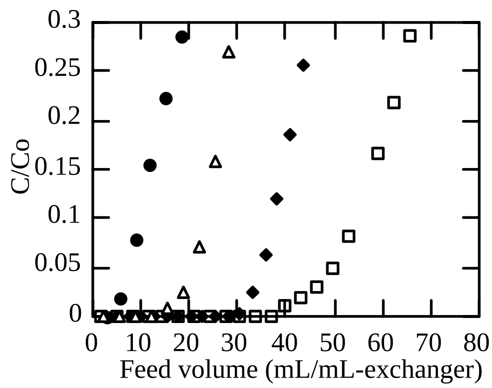


Fig. 1. Breakthrough profiles of Cu(II) in column mode uptake of Cu(II) by phosphonate fibers and resin.
(◆) RCSP 10 h^{-1}, (●) RCSP 500 h^{-1}.
(□) FCPS 1000 h^{-1}. (Δ) FCP 1000 h^{-1}.

References

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