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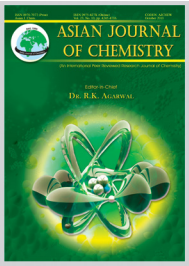

Preparation and Application Progress of Polyethylene Hollow Fiber Ion-Exchange Membrane

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In the paper, preparations of polyethylene hollow fiber ion-exchange membranes are described. Generally, the preparations consist of three steps: First, free radicals are produced on the surface of polyethylene hollow fiber membranes using γ-ray or electron beam. Second, pre-functional groups are introduced when monomer reacts with free radicals. Finally, polyethylene hollow fiber ion-exchange membranes are produced when reagents react with pre-functional groups. In addition, applications of membranes in the protein separation, metal ion removal and enzyme immobilization are also described, which is helpful to research on preparations of hollow fiber ion-exchange membranes for other materials.

Key Words: Membrane, Protein separation, Metal ion removal, Enzyme immobilization.

INTRODUCTION

Polyethylene hollow fiber membranes have excellent mechanical property, chemical property, permeability, and they can be used for gas separation. However, their low surface energy and high hydrophobicity result in low water flux, short service life and high operation cost, which can restrict their applications. To improve their performances and expand application areas, preparations of polyethylene hollow fiber ion-exchange membranes are very effective. That is because hollow fiber ion-exchange membranes have not only advantages of hollow fiber membranes such as simple structure and small device but also good selective permeability. As polyethylene material with ion-exchange groups is strongly hydrophilic, hollow fiber ion-exchange membranes are difficult to be produced by direct spinning. Therefore, preparations of polyethylene hollow fiber ion-exchange membranes consist of three steps: base membrane preparation, introduction of pre-functional groups and introduction of ion-exchange groups.

In this article, preparations of polyethylene hollow fiber anion-exchange membranes, polyethylene hollow fiber cation-exchange membranes, polyethylene hollow fiber amphoteric membranes from polyethylene hollow fiber membrane will be described and their applications in the protein separation, metal ion removal and enzyme immobilization will be also introduced.

EXPERIMENTAL

Polyethylene hollow fiber anion-exchange membranes: Generally, preparations of polyethylene hollow fiber anion-exchange membranes consist of three steps: First, free radicals are produced on the surface of polyethylene hollow fiber membrane using electron beam. Second, pre-functional groups are introduced when monomer reacts with free radicals. Finally, polyethylene hollow fiber anion-exchange membranes are produced when reagents react with pre-functional groups. For example, Kubota *et al.*[1] prepared polyethylene hollow fiber anion-exchange membranes containing ethanolamino groups through three steps: (1) Irradiation of an electron beam onto the porous polyethylene hollow fiber membrane. (2) Graft polymerization of glycidyl methacrylate (GMA) onto the irradiated porous hollow fiber membrane in the liquid phase. (3) Addition of ethanolamine to the epoxy groups. Preparations of polyethylene hollow fiber anion-exchange membranes by Ozawa *et al.*[2] also consist of three steps: (1) The polyethylene hollow fiber was irradiated with an electron beam using a cascade-type accelerator to produce radicals. (2) GMA was grafted to the hollow fiber to append the epoxy groups. (3) The epoxy groups were converted to four kinds of functional groups. Tsuneda *et al.*[3] prepared polyethylene hollow fiber anion-exchange membranes through four steps: (1) The polyethylene hollow fiber was irradiated with an electron beam from an accelerator under a nitrogen atmosphere. (2) The irradiated hollow fiber was immersed in GMA solution. (3) The epoxy groups produced were converted into diethylamino (DEA) groups by immersing the GMA-grafted hollow fiber in aqueous diethylamine solution. (4) The remaining epoxy groups were subsequently converted into ethanolamino (EA) groups by soaking the hollow fiber in ethanolamine. More

preparation methods of polyethylene hollow fiber anion-exchange membranes are summarized in Table-1.

TABLE-1
PREPARATION METHODS OF PE HOLLOW FIBER ANION-EXCHANGE MEMBRANES

Preparation steps	Preparation methods of free radicals	Reagents for functional group reaction	References
3	Electron beam	*N*-methylglucamine; 3-amino-1,2-propanedio	4
3	Electron beam	Alkylamine	5
3	Electron beam	*N*-methylglucamino	6
4	Electron beam	Diethylamine; Ethanolamine	7
3	Electron beam	Iminodiethanol	8
3	Electron beam	Diethanolamine; Diis-opropanolamine; *N*-methylglucamine; 3-amino-1,2 propanediol	2
3	Electron beam	Diethylamine	9
3	Electron beam	Diethylamine	10
4	Electron beam	Diethylamine; Ethanolamine	11
4	Electron beam	Diethylamine; Ethanolamine	12
3	Electron beam	Diethylamine; Ethanolamine	13
4	Electron beam	Diethylamine; Ethanolamine	14
4	Electron beam	Diethylamine; Ethanolamine	15

RESULTS AND DISCUSSION

As is shown in Table-1, free radicals are almost produced by electron beam in the preparation process of polyethylene hollow fiber membranes, and preparation steps are three or four. In addition, reagents for functional group reaction are diethylamine, ethanolamine and iminodiethanol.

Polyethylene hollow fiber cation-exchange membranes: Similar to preparations of polyethylene hollow fiber anion-exchange membranes, preparations of polyethylene hollow fiber cation-exchange membranes consist of three steps. For example, Miyoshi *et al.*[16] prepared polyethylene hollow fiber cation-exchange membranes containing sulfonic acid groups according to the following three steps: (1) Irradiation of an electron beam onto the starting porous hollow-fiber membrane to produce radicals. (2) Graft polymerization of GMA to generate the graft chain. (3) Addition of taurine to the epoxy group of the graft chain. More preparation methods of polyethylene hollow fiber cation-exchange membranes are summarized in Table-2.

As is shown in Table-2, free radicals are almost produced by electron beam or γ-ray in the preparation process of polyethylene hollow fiber membranes, and preparation steps are three or four. In addition, reagents for functional group reaction are sodium sulfite, sulfuric acid and chlorosulfonic acid.

Polyethylene hollow fiber amphoteric membranes: Similar to preparations of polyethylene hollow fiber anion-exchange or cation-exchange membranes, preparations of polyethylene hollow fiber amphoteric membranes also consist of three or four steps, but researches on polyethylene hollow fiber amphoteric membranes are less than those on the former two membranes. For example, Iwanade *et al.* prepared polyethylene hollow fiber amphoteric membranes according to the following three steps: (1) Irradiation with an electron beam: the porous hollow fiber membrane was irradiated with an electron beam. (2) Grafting of GMA: the irradiated hollow fiber was immersed in GMA/methanol solution. (3) Introduction of three kinds of amphoteric groups into the epoxy group: the GMA-grafted hollow fiber was immersed in an ampholite solution. (4) Conversion of the remaining epoxy group into a diol group: the hollow fiber was immersed in sulfuric acid.

TABLE-2
PREPARATION METHODS OF PE HOLLOW FIBER CATION-EXCHANGE MEMBRANES

Preparation steps	Preparation methods of free radicals	Reagents for functional group reaction	References
4	Electron beam	Sodium sulfite; water	17
3	γ-ray	Chlorosulfonic acid	18
4	Electron beam	Sodium sulfite; sulfuric acid	19
4	Electron beam	Sodium sulfite; sulfuric acid	20
4	Electron beam	Sodium sulfite; water	21

Applications of polyethylene hollow fiber ion-exchange membranes: As polyethylene hollow fiber ion-exchange membranes have charged groups, their applications have extended to many areas such as protein separation and purification, heavy metal ion removal and enzyme immobilization.

Protein separation and purification: As an important complex biological macromolecule, protein has many applications in medicine, biology and engineering, and membrane separation has a great effect on protein. Polyethylene hollow fiber ion-exchange membranes, important membranes in the field of membrane separation, have been widely used by many domestic and foreign researchers. For example, Kubota *et al.*[1] introduced ethanolamino groups into polyethylene hollow fiber membranes by chemical modification and prepared polyethylene hollow fiber anion-exchange membranes through three steps. Then, the prepared membranes were used for the recovery of bovine serum albumin and the results showed that they had a good separation. Iwanade *et al.*[22] introduced amphoteric groups into polyethylene hollow fiber membrane by chemical modification and prepared polyethylene hollow fiber amphoteric membranes through four steps. Then, the prepared membranes were used for protein purification and the results showed that the purification effect was good.

Heavy metal ion removal: Heavy metals include heavy metal ions and their compounds, especially they refer to significantly toxic metals such as copper, mercury, cadmium and lead. When heavy metals come into the environment, they will be very toxic to organisms. Therefore, heavy metals should be removed before discharge and polyethylene hollow fiber ion-exchange membranes have been widely used in this field. For example, Kim and Saito[19] introduced sulfonic acid groups

to polyethylene hollow fiber membranes by chemical modification and prepared polyethylene hollow fiber cation-exchange membrane. To investigate the capability of heavy metal removal, lead ion was used as a model metal ion and the results showed that the prepared hollow fiber ion-exchange membranes had high ion-exchange capacity (3.8 mmol/g) and the removal of lead ion had good results. Kawakita *et al.*[6] chemically modified polyethylene hollow fiber membrane and introduced strong basic ion-exchange groups and prepared polyethylene hollow fiber anion-exchange membranes. Then, they were used to remove antimony and the results showed that the effect of heavy metals removal is good.

Enzyme immobilization: Enzymes are proteins with special catalytic capabilities and have been widely used in food industry. However, there are still some problems such as high cost of enzyme separation, instability of free enzyme, which limit the applications of the enzymes. For solving the problems, Kawai *et al.*[15] introduced diethylamino groups and ethanolamino groups into polyethylene hollow fiber membranes and prepared polyethylene hollow fiber anion-exchange membrane through four steps. Then, they were used for aminoacylase immobilization and the results showed that the prepared membranes had good effect of enzyme immobilization. Goto *et al.*[9] introduced diethylamino groups into polyethylene hollow fiber membranes and prepared anion-exchange membrane successfully. When they were used for enzyme immobilization, the results showed the prepared membranes had excellent effect of enzyme immobilization (4.26×10^{-2} kg/ kg membrane).

Conclusion

Polyethylene hollow fiber ion-exchange membranes have not only advantages of hollow fiber membranes such as simple structure and small device but also selective permeability. In this paper, preparation methods, preparation process, reagents and applications of polyethylene hollow fiber ion-exchange membranes are described, which is helpful to research on preparations of hollow fiber ion-exchange membranes for other materials.

REFERENCES

1. N. Kubota, S. Miura, K. Saito, K. Sugita, K. Watanabe and T. Sugo, *J. Memb. Sci.*, **117**, 135 (1996).
2. I. Ozawa, K. Saito, K. Sugita, K. Sato, M. Akiba and T. Sugo, *J. Chromatogr. A*, **888**, 43 (2000).
3. S. Tsuneda, K. Saito, S. Furusaki and T. Sugo, *J. Chromatogr. A*, **689**, 211 (1995).
4. T. Saito, H. Kawakita, K. Uezu, S. Tsuneda, A. Hirata, K. Saito, M. Tamada and T. Sugo, *J. Memb. Sci.*, **236**, 65 (2004).
5. S. Domon, S. Asai, K. Saito, K. Watanabe and T. Sugo, *J. Memb. Sci.*, **262**, 153 (2005).
6. H. Kawakita, K. Uezu, S. Tsuneda, K. Saito, M. Tamada and T. Sugo, *Hydrometallurgy*, **81**, 190 (2006).
7. K. Hagiwara, S. Yonedu, K. Saito, T. Shiraishi, T. Sugo, T. Tojyo and E. Katayama, *J. Chromatogr. B*, **821**, 153 (2005).
8. S. Nishiyama, K. Saito, K. Saito, K. Sugita, K. Sato, M. Akiba, T. Saito, S. Tsuneda, A. Hirata, M. Tamada and T. Sugo, *J. Memb. Sci.*, **214**, 275 (2003).
9. M. Goto, T. Okubo, H. Kawakita, K. Uezu, S. Tsuneda, K. Saito, M. Goto, M.o Tamada and T. Sugo, *Biochem. Eng. J.*, **37**, 159 (2007).
10. H. Kawakita, K. Sugita, K. Saito, M. Tamada, T. Sugo and H. Kawamoto, *J. Memb. Sci.*, **205**, 175 (2002).
11. N. Kubota, Y. Konno, K. Saito, K. Sugita, K. Watanabe and T. Sugo, *J. Chromatogr. A*, **782**, 159 (1997).
12. S. Tsuneda, H. Kagawa, K. Saito and T. Sugo, *J. Colloid. Interf. Sci.*, **176**, 95 (1995).
13. M. Nakamura, S. Kiyohara, K. Saito, K. Sugita and T. Sugo, *Anal. Chem.*, **71**, 1323 (1999).
14. K. Sunaga, M. Kim, K. Saito, K. Sugita and T. Sugo, *Chem. Mater.*, **11**, 1986 (1999).
15. T. Kawai, M. Nakamura, K. Sugita, K. Saito and T. Sugo, *Biotechnol. Progr.*, **17**, 872 (2001).
16. K. Miyoshi, K. Saito, T. Shiraishi and T. Sugo, *J. Memb. Sci.*, **264**, 97 (2005).
17. K. Saito, *Sep. Sci. Technol.*, **37**, 535 (2002).
18. S. Choi and Y.C. Nho, *J. Appl. Polym. Sci.*, **71**, 2227 (1999).
19. M. Kim and K. Saito, *Radiat. Phys. Chem.*, **57**, 167 (2000).
20. N. Sasagawa, K. Saito, K. Sugita, S. Kunori and T. Sugo, *J. Chromatogr. A*, **848**, 161 (1999).
21. T. Kawai, K. Sugita, K. Saito and T. Sugo, *Macromolecules*, **33**, 1306 (2000).
22. A. Iwanade, D. Umeno, K. Saito and T. Sugo, *Biotechnol. Progr.*, **23**, 1425 (2007).