The pH Dependence of Poly(acrylic acid)-graft-Polypropylene Hollow Fiber Membrane

LIU Yan-jun[1,2], LIU Chun-ying[2], CHEN Rui[1], FU Xue-qi[1]
(1. Environmental Science and Engineering College, NanKai University, Tianjin 300071, China;
2. Tianjin Polytechnic University, Tianjin 300160, China)

Abstract: The pH dependence of poly(acrylic acid)-graft polypropylene membranes were evaluated. The result shows that pH sensitivity of grafted membranes increases with the rise of grafting degree (dg) as dg< 17%. For the microfiltration of Bovine serum albumin (BSA) solution, all membranes show the most serious fouling behavior at pH 4.7 (the isoelectric point IEP of BSA) and the smallest flux decline at pH 3. Compared with the ungrafted PP membrane, grafted membranes show more serious fouling behavior at pH 3, whereas 18% grafted membrane has a certain antifouling behavior at pH 4.7 and 8. It has been shown that the electrical interactions and the conformation of BSA and grafted chains should be considered to analyze the fouling behavior.

Key words: pH sensitivity; water permeability; Bovine serum albumin; microfiltration
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The pH sensitive membrane that can response to pH stimulus has been extensively studied[1-3]. These membranes have been expected many potential applications ranging from selective separations[1] to controlled-released systems[2]. pH-sensitivity membranes were reported an alleviated fouling behavior for the microfiltration of drinking water[3]. In this work, the pH-sensitivity and the BSA microfiltration of poly(acrylic acid)-graft polypropylene membranes were studied.

1 Experimental

1.1 Materials

The poly(acrylic acid)-graft polypropylene membranes were prepared by UV-photografting[3].

1.2 The microfiltration experiments

The microfiltration experiments were carried out at 25±2 ℃ under a transmembrane pressure of 100 kPa with a flow rate of 100 L/h. Membranes were wetted with 70% ethanol solution in advance.

2 Results and discussion

2.1 pH sensitivity of water permeability

In Fig.1, due to the non-ionizability of PP membrane, it has no response to pH. While the conformation of the polyacrylic acid (PAA) chains on grafted membranes changes from coiled at low pH to extended at high pH[2]. Thus, an increase in pH results in dramatic flux decline from the maximum at pH 1 to the minimum at pH 11.

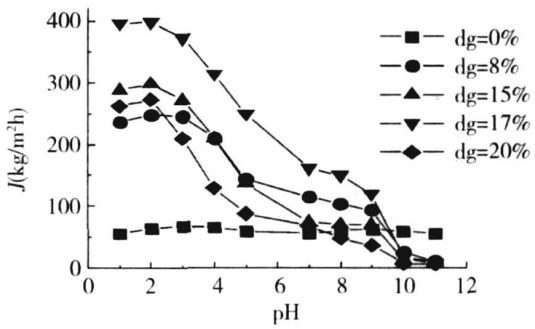

Fig.1 Flux-pH dependence of membranes

According to the Hagen-poiseuille law[4], the changing ratio $N_{7/11}$ of pore size as pH was altered from 1 to 11 was calculated as follow:

$$N_{7/11}=\frac{r_{pH7}}{r_{pH11}}=\left(\frac{J_{pH7}}{J_{pH11}}\right)^{\frac{1}{4}}$$

From Fig.2, as dg< 17%, $N_{7/11}$ increases with the rise of dg, which indicates pH sensitivity of grafted membranes is improved. Whereas as dg> 17%, many pores are constricted or blocked by PAA chains[2], which causes a loss on pH sensitivity. The curve of $N_{7/10}$ is higher than that of $N_{7/1}$, which means grafted membranes are more sensitive in alkaline solution due to the swift rise of charge density.

2.2 Membrane fouling during BSA microfiltration

From Fig.3: ① All membranes show the most

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作者简介: 刘燕军 (1972年生), 女, 副研究员; 通讯联系人: 傅学起; E-mail: fuxueqi@nankai.edu.cn

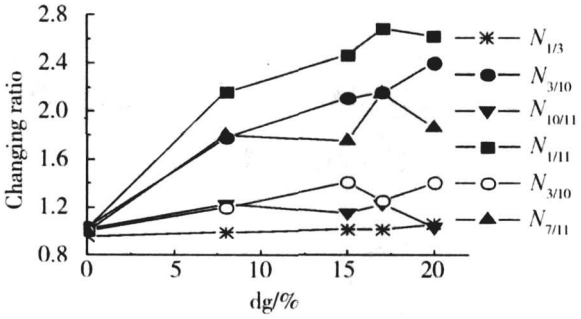

Fig. 2　Changing ratios in different pH ranges

pronounced flux decline driven by the hydrophobic interactions between BSA and membrane at pH 4.7. The hydrophilic surface of grafted membranes alleviates the absorption of BSA, so the larger dg leads to the slower flux decline. ② At pH 3, 5% PAA chains dissociate and attract the positive BSA. So the higher of dg, the worse fouling is. ③ After grafting, membrane surface becomes coarser, which provides more absorbing position for BSA. At pH 8, the repulsive force between PAA and BSA can overcome this effect at high dg. As a result, 18% grafted membrane has an antifouling behavior.

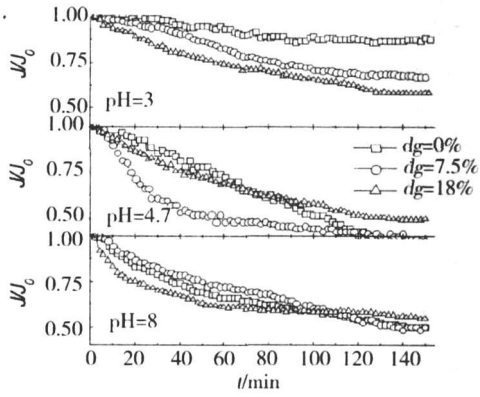

Fig. 3　The BSA filtration behavior of membranes

In alkali solution, BSA molecule has more hydrophobic surface[5] and is easier to aggregate on membrane surface. As a result, the BSA fouling to membranes is more serious in alkaline solution.

3　Conclusion

(1) The pH sensitivity of grafted membranes increase with the rise of grafting degree as dg≤17%.

(2) All membranes have the most serious fouling at pH 4.7 and followed by pH 8. At pH 3, more fouling takes place for grafted membranes. At pH 4.7 and 8, 18% grafted membrane presents certain antifouling behavior.

(3) The electrostatic interaction and the conformation of BSA and the membrane surface are the main factor affecting membrane fouling.

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聚丙烯接枝聚丙烯酸中空纤维膜的 pH响应性

刘燕军[1,2]，吕春英[2]，陈　蕊[1]，傅学起[1]

(1. 南开大学环境科学与工程学院，天津 300071；2. 天津工业大学材料化工学院，天津 300160)

摘　要：评价了聚丙烯酸接枝改性聚丙烯中空纤维膜的 pH响应性。在接枝率小于 17%时，接枝膜的 pH敏感性随接枝率的增加而提高。在牛血清蛋白 (BSA) 溶液微滤试验中，接枝膜与未接枝膜在 BSA的等电点 4.7处，都表现出严重的膜污染；而 pH=3时，膜通量下降趋势最小。与未接枝膜相比，接枝膜在 pH=3时污染较严重，而接枝率 18%的膜在 pH 4.7和 8时表现出一定的抗污染性。研究表明：蛋白质与膜之间的电荷作用以及 BSA和膜构象的变化都是膜污染的重要影响因素。

关键词：pH敏感性；水渗透性；牛血清蛋白；微滤

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