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Synthesis and Adsorption Property of Dihydroxyl Azacrown Ether-Grafted Chitosan

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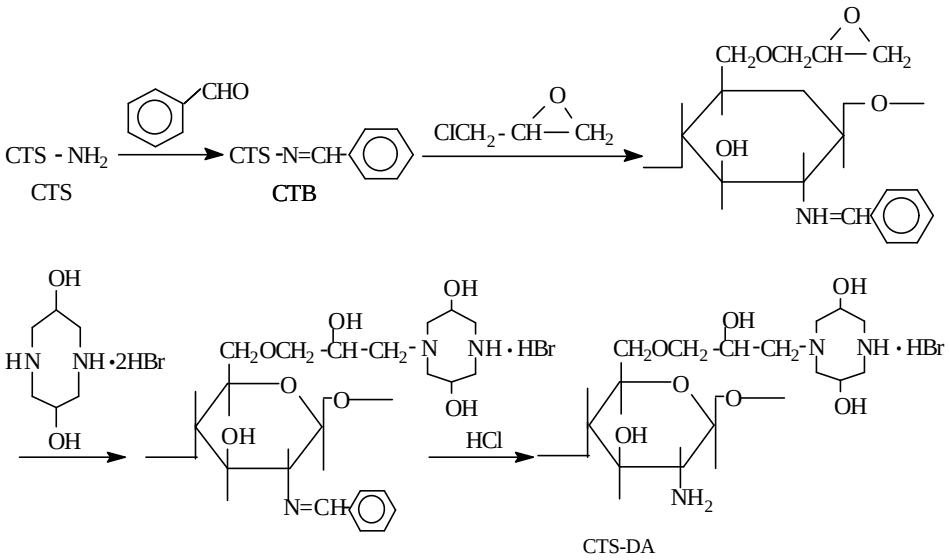
Abstract: A novel dihydroxyl azacrown ether chitosan was synthesized by reacting dihydroxyl azacrown ether with epoxy activated chitosan. The adsorption property of the azacrown ether chitosan for Pb^{2+}, Cr^{3+}, and Ag^{+}, were determined. The experimental results showed that the dihydroxyl azacrown ether grafted chitosan has high adsorption capacity and high selectivity for some metal ions.

Keywords: Chitosan, azacrown ether, adsorption property, synthesis.

Chitin is one of the most abundant organic materials that can be easily obtained in nature. Chitosan (CTS), which is easily derived from chitin by N-deacetylation. Chitosan has both hydroxyl and amine groups that can be modified to prepare chitosan derivatives. Several processes have been proposed to modify chitosan by grafting new functional groups on the polymer backbone. These operations allow the polymer porosity to be enhanced, and the uptake capacity and the selectivity to be increased[1,2].

Azacrown ethers are new functional compounds. They have specific complex selectivity and stability for many heavy/precious metal ions[3], but their solubility is too great to recover after being used; therefore, their application is limited. If azacrown ethers were grafted in a polymer, then, it will give polymerized azacrown ethers containing double structures and properties. We have already reported a series of chitosan azacrown ethers[4-6], the present study aimed to prepare the novel chitosan azacrown ether bearing two hydroxyl groups and to investigate their properties.

The C-2 amino group in chitosan was protected by the reaction between benzaldehyde and chitosan to form N-benzylidene chitosan (CTB), and the CTB was activated with epichlorohydrin to give epoxy chitosan- benzylidene (EACT). After the novel chitosan azacrown ether bearing dihydroxyl group (CTS-DH) was obtained through the reaction of EACT with 3,7-dihydroxyl-1,5-diazacyclic octane dihydrobromic acid, the Schiff base was decomposed by reacting the intermediate and ethanol solution of dilute hydrochloride. The reaction procedures are as follows.



Compound **CTS-DA**: $C_{15}H_{28}N_3O_7Br$, light yellow powder, yield 82.35%. Analytical data: calc.: C 22.30, H 10.78, N 15.61; found: C 21.14, H 9.87, N 14.62. It can be seen that the contents of C, N, and H were lower than that of calculation. The reason is that the percent of the graft yield for CTS-DA is not 100%, but 97.63%. IR (KBr, cm^{-1}): 1600, 1480, 1080, 3385; X-ray (WAXD): $2\theta = 20^{o}$; ^{13}C NMR (solid-state, ppm): 59 (-CH_2-, m), 42 (-CH_2-N-, m).

The adsorptive and selective properties of the dihydroxyl azacrown ether chitosan for some metal ions were investigated. The adsorption capacity of Ag^{+}, Pb^{2+}, and Cr^{3+} are 0.67 mmol·g^{-1}, 0.52 mmol·g^{-1}, and 0.45 mmol·g^{-1}, respectively. The selectivity coefficients of CTS-DA are $K_{Ag(I)/Pb(II)}$ = 17.85, $K_{Ag/Cr(III)}$ = 14.54 in an aqueous system containing Ag^{+}- Pb^{2+}- Cr^{3+}. The experimental results demonstrated that the azacrown ether could raise the adsorption ability of chitosan for some metal ions. Therefore, we expect that the novel grafted chitosan azacrown ether will have wide application for the separation and concentration of heavy metal.

References

1. K. inoue. Y. Baba. K. Yoshiguza, *Bull Chem. Soc. Jpn.*, **1993**, *66*, 2915.
2. E. Piton. M. Acuminate. A. Pomaded, *Langmuir*, **1997**, *13*, 1653.
3. R. M. Izaatl, *Chem. Rev*., **1985**, *85*, 271.
4. Z. K. Yang. Y. T. Wang. Y. R. Tang, *J. Appl. Polym. Sci.*, **1999**, *74*, 3063.
5. Z. K. Yang. Y. T. Wang. Y. R. Tang, *J. Appl. Polym. Sci*., **2000**, *75*, 1255.
6. Z. K. Yang. Y. Yuan. Y. T. Wang, *J. Appl Polym. Sci*., **2000,** *77*, 93.

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