学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Study on synthesis of ß-cyclodextrin linked chitosan derivatives with different linkers and removal of dyes
（リンカー鎖長の異なるβ - シクロデキストリン結合キトサン誘導体の合成と色素の除去に関する研究）

The remaining synthetic dyes from different sources, *e.g.*, textile industries, leather tanning, paper and printing production, and food technology, are considered as hazardous pollutants introduced into natural water. Most of these dyes are toxic and potentially carcinogenic. The dyes removal from industrial effluents is one of the major considerations for environmental conservation. Recently, biomaterials have been widely used for removing organic pollutants from wastewater. Cyclodextrins (CDs), cyclic oligosaccharides consisting of 6-8 D-glucopyranose units through α-(1,4) glycosidic bonds, are regarded as a family of the most characterized supramolecular host compounds. The characteristic feature of these compounds is mainly based on the rigidity and chirality of the internal hydrophobic cavity, and provides a remarkable capacity to form inclusion complexes with various guest molecules , especially aromatics, in aqueous solution. Chitosan has been regarded as a highly attractive and versatile biomaterial because of its unique polycationic property. In order to create effective adsorbent material for the removal of dyes from water, β-CD linked chitosan derivatives having different linkers of C0 and C4 units were synthesized and subjected to inclusion property analysis. This thesis describes the preparation procedure of two different β-CD linked chitosan derivatives, their structure analysis, and characterization of inclusion complex between both derivatives and various dyes by fluorescence and ^{1}H NMR spectroscopy. Furthermore, practical application to removal process of dye pollutants is discussed.

Chapter 1 describes general introduction about the purpose, scope, and contents of the present study on β-CD linked chitosan material for dye adsorption.

Chapter 2 described the synthesis of β-CD linked chitosan derivatives with and without a linking moiety of C4 unit performed by reductive alkylation of amino group of chitosan with β-CD aldehyde derivatives, gave two β-CD linked chitosan derivatives with C4 (4-butylamido) and C0 linking arms. The degree of substitution (D.S.) of both C4-β-CD and C0-β-CD linked chitosan was controlled by the ratio of starting materials. The structures of the products were confirmed by ^{1}H and ^{13}C NMR. Their inclusion properties of C4-β-CD (D.S. 18%) and C0-β-CD linked chitosan (D.S.17%) using a fluorescent probe, 6-(*p*-toluidino)-2-napthalene-6-sulfonate (TNS), were investigated using fluorescent spectroscopy in acetate buffer (pH 4.3) at 25°C. Among two β-CD linked chitosan derivatives, continuous variation of Job`s method revealed that only C4-β-CD linked chitosan maintained 1:1 stoichiometry of inclusion complex with TNS. The stability constant of the

inclusion complex with C4-β-CD linked chitosan and TNS determined by Benesi-Hildebrand plot was 2.3×10^{3} M^{-1}.

Chapter 3 described the results of the investigation of inclusion ability of original β-CD, C4-β-CD and C0-β-CD linked chitosan in order to obtain basic information of adsorption mechanism of CD-linked chitosan. TNS and some dyes were used as guest compounds and analysis was performed by ^{1}H NMR spectroscopy. As a result, Job's plots between TNS and both original β-CD and synthetic C4-β-CD linked chitosan were also shown 1:1 stoichiometry. In contrast to them, C0-β-CD linked chitosan showed different stoichiometry, which was accordance with fluorescence spectroscopic analysis. Furthermore, chemical shift change of protons of the guest compound suggested conformation of the inclusion complex and possibility of ionic interaction between chitosan amino group and sulfonate group of TNS.

Chapter 4 described the results of the basic investigation toward practical application of dye removal. The adsorption experiments were carried out using two anionic dyes, reactive black 5 (RB5) and reactive orange 16 (RO16) and cross-linked insoluble material of β-CD linked chitosan. Results of batch removal experiments showed the effective adsorption against RB5 and RO16 in aqueous solution at pH 3. The adsorption isotherms were revealed that Langmuir equation was fitted with RB5 and Freundlich equation was fitted with RO16. These results suggested that the adsorption occurred on the surface of the material and controlled by the formation of an inclusion complex with the CD residue and ionic-exchange interaction with the amino group of chitosan. The kinetics data of both dyes were well fitted to the pseudo-second order adsorption process. These data suggested that cross-linked β-CD linked chitosan can be effectively used as an adsorbent for removal of dyes and its capacity is depended on operating variables, such as pH, contact time and initial dye concentration.

In conclusion, the two difference linking arms, C0-β-CD and C4-β-CD linked chitosan, have been synthesized. Their inclusion properties with fluorescence probe (TNS) were investigated using fluorescent titration and ^{1}H NMR titration. The inclusion complex of C4-β-CD linked chitosan (D.S. 18%) was 1:1 stoichiometry. This is probably due to the hydrophobic interaction of β-CD molecules and ionic interaction of chitosan structure. Nevertheless, the main interaction of C0-β-CD linked chitosan was ionic interaction between amino group of chitosan and TNS molecules due to the gelation solubility of material. Besides the Cross-linked β-CD linked chitosan were successfully used in adsorption of anionic dyes, their application could be used for removal others organic pollutants from wastewater.