

β -cyclodextrin inclusion properties with guest molecules using hetero-bi-functional reactive dye

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Abstract— Cyclodextrin is a cyclic oligosaccharid material which shows an ability to incorporate organic guest molecules inside their cavity area. Thus, this β -cyclodextrin treatment on fiber substrates may provide the changed surface characteristics of the substrates such as solubility, chemical reactivity and spectral property. In this context, the aim of this present work is to make a bridge connection using hetero-bi-functional reactive dye between fiber substrates and β -cyclodextrin. In addition, the corresponding Berberine inclusion behaviors into the inner cavity of β -cyclodextrin was examined. The %exhaustion of Berberine inclusion as a guest molecule within the β -cyclodextrin was measured using UV-Vis spectrophotometer. The findings showed that the %exhaustion of Berberine inclusion increased with increasing the prepared dye bridge compound and β -cyclodextrin host material.

Keywords: β -cyclodextrin, berberine, dye bridge, hetero-bi-functional reactive dye, guest molecule

1. Introduction

Developments in textile finishing technology have recently focused on the incorporating of additional functional properties and benefits into fibers and garments. To incorporate anti-bacterial agent, aroma and perfume into textiles are good examples for functional treatment process.

It is well known that β -cyclodextrin is a toroidal shape polysaccharide which is made up of six to eight D-glucose monomers being connected at 1 and 4 carbon atoms^{1,2)}.

The structure of β -cyclodextrin is schematically represented in Fig. 1. The cavity of β -cyclodextrin shows relatively hydrophobic property, while the external face represents hydrophilic characteristic. Its shape is capable of forming inclusion complexes with coming guest organic molecules.

This β -cyclodextrin treatment on fiber substrates may provide the changed surface characteristics of

the substrates such as solubility, chemical reactivity and spectral property³⁻⁷⁾. To make an attachment of β -cyclodextrin to the cellulosic fibers, the hetero-bi-functional dye was used as a bridge agent. It is well known that hetero-bi-functional reactive dye, which contains two different types of reactive group, has been attracted by many important dyeing and finishing research areas⁸⁻¹⁰⁾. Using these two reactive groups, the dye was considered as a bridge performing material, connecting cellulosic fiber substrates and β -cyclodextrin.

In this context, the aim of this present work is to examine the %exhaustion behaviors of Berberine colorant inclusion as a guest material and to study the effect of both β -cyclodextrin and hetero-bi-functional reactive dye on %exhaustion of Berberine inclusion. The %exhaustion of Berberine inclusion was then measured with UV-Vis spectrophotometer. If Berberine could be complexed within the anchored β -cyclodextrin's

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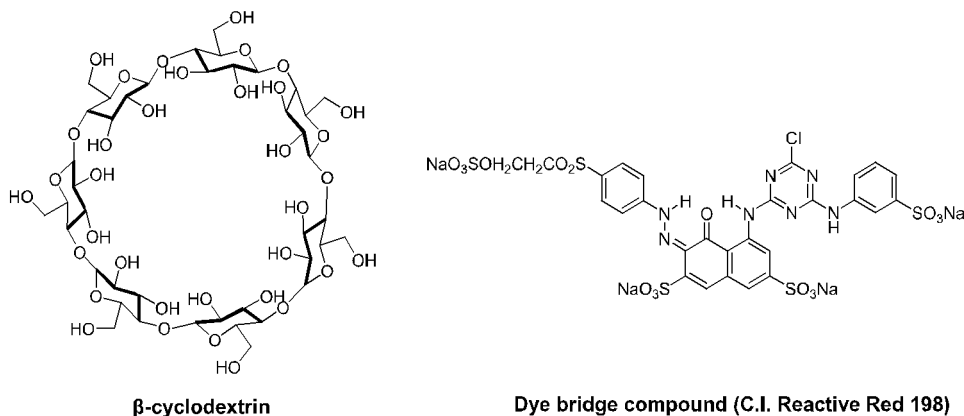


Fig. 1. The structure of β -cyclodextrin and dye bridge.

inner cavity on cellulosic substrates, %exhaustion of Berberine would be increased with increasing the concentration of β -cyclodextrin host and dye bridge.

2. Experimental

2.1 Reagents and Materials

All chemicals used were of analytical grade and double distilled water was used. Cellulosic substrates were purchased from Korea Apparel Testing and Research Institute (KATRI). The β -cyclodextrin (Fig. 1) was purchased from Aldrich Chemical Co. The hetero-bi-functional reactive dye used as a bridge material on cellulosic substrates was C. I Reactive Red 198.

2.2 Measurements

A TU-1800 PC UV/Vis spectrophotometer was used for measuring the absorption spectra. A Corning model 220 pH meter was used for pH measurements.

2.3 Initial study for Berberine inclusion

β -cyclodextrin concentration was used to be ranging from zero to $1.04 \times 10^{-3}\text{M}$ and Berberine concentration was maintained at $2.0 \times 10^{-5}\text{M}$. To find out the effect of Berberine inclusion complex inside β -cyclodextrin cavity according to the variation of β -cyclodextrin concentration, %exhaustion was determined. The effect of pH using Mallvaine buffer solution (pH 4-8) was also studied.

2.4 Dye and β -cyclodextrin linkage formation

Cellulosic fibers (2.5g) were dyed with various concentrations of hetero-bi-functional reactive dye and β -cyclodextrin using 20 g/l NaCl at pH 7 in a sealed, stainless steel dye pots of 120 cm³ capacity laboratory-scale dyeing machine (ACE-6000T). Samples were placed at 45 °C dye bath for 30 min, and pH was then adjusted. Temperature was raised until it reaches 80 °C by 2 °C/min and then continued for 45min.

The dyed samples were washed off using 2 g/l Na_2CO_3 and 2 g/l of a non-ionic surfactant at 60 °C for 30min. Fig. 2 shows the reaction scheme of the treatment of dye bridge compound and β -cyclodextrin onto cellulosic substrates.

2.5 Berberine inclusion

Berberine as a guest molecule was complexed within the β -cyclodextrin's inner cavity. The %exhaustion of Berberine inclusion was proportional to the pretreated β -cyclodextrin

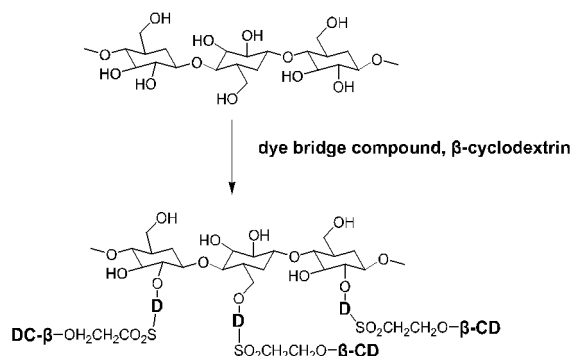


Fig. 2. Reaction scheme of dye bridge and β -cyclodextrin anchor.

concentration. The concentration of Berberine used was 2×10^{-5} M. The exhaustion rate (%E) was then calculated using equation (1):

$$\%E = \frac{[D_o - D_t]}{D_o} \times 100 \quad (1)$$

where D_0 and D_t are the quantity of dye in the initial and final bath, respectively. Those values were calibrated through absorbance measurement of original and exhausted bath.

3. Results and Discussion

3.1 Initial study for inclusion complex formation

An initial study is to examine the effect of β -cyclodextrin on the %exhaustion of Berberine inclusion. Also, the effects of pH on the %exhaustion of Berberine inclusion were determined. The UV-vis spectra of Berberine at various concentrations of β -cyclodextrin are shown in Fig. 3. In this case, when β -cyclodextrin was added into the Berberine solution, the general decreasing trend in absorbance of Berberine was shown with increasing the concentration of β -cyclodextrin. This finding displays that Berberine is being complexed inside β -cyclodextrin's cavity space. Thus, the corresponding the spectral peaks were getting decreased with increasing Berberine complex inclusion. Fig. 4 shows that %exhaustion of Berberine inclusion increased with increasing the pH. However, the higher %exhaustion of Berberine inclusion decreased after maximum

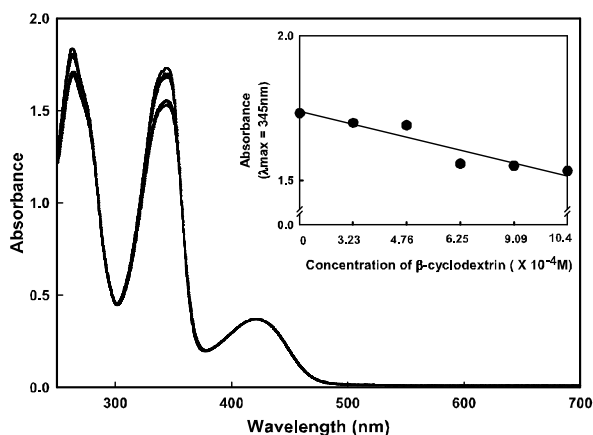


Fig. 3. UV-Vis absorption spectra of Berberine at various concentration of β -cyclodextrin.

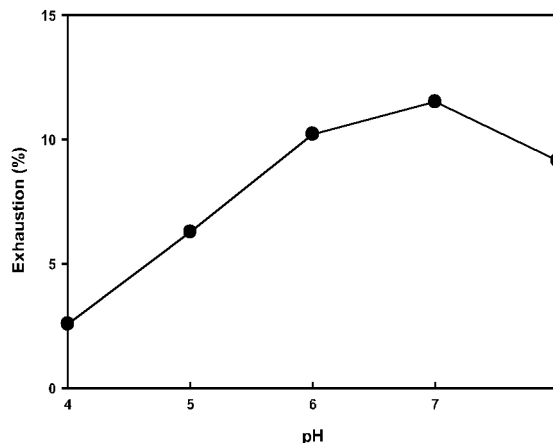


Fig. 4. Effect of pH on the %exhaustion of Berberine inclusion.

value of pH 7. With these results, it could be proposed that an acidic or alkaline condition tends to interfere the inclusion of β -cyclodextrin with Berberine.

3.2 Effect of β -cyclodextrin on the %exhaustion of Berberine inclusion within the fibers

Anchoring β -cyclodextrin to the cellulosic substrates is a function to provide inclusion potentials towards the guest molecule of Berberine colorant.

This function was utilized with hetero-bi-functional reactive dye as a bridge agent between β -cyclodextrin and cellulosic substrates.

β -cyclodextrin molecules can be anchored to one of the reactive groups of hetero-bi-functional reactive dye, while the other reactive group of the dye is able to link with hydroxyl groups on cellulosic fiber molecules. Fig. 5 shows the effects of β -cyclodextrin concentration on the %exhaustion of Berberine inclusion within the cellulosic substrates. Also, the effects of dye bridge concentration on the %exhaustion of Berberine inclusion are shown in Fig. 6. From the results, it can be proposed that the %exhaustion of Berberine inclusion is dependent on the concentration of both β -cyclodextrin and dye bridge within the cellulosic substrates. Thus, the %exhaustion of Berberine inclusion increased with increasing the concentration of both β -cyclodextrin and hetero-bi-functional reactive dye.

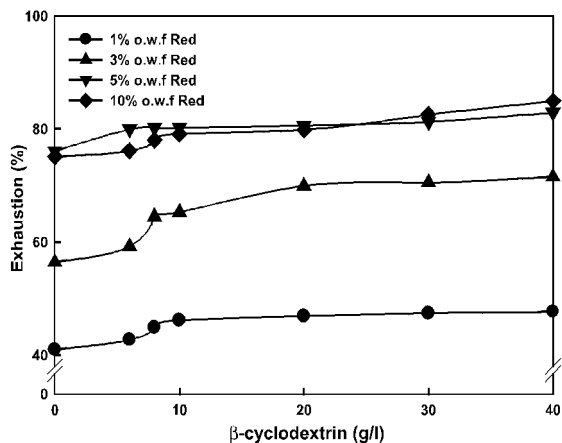


Fig. 5. Effect of β -cyclodextrin concentration on the %exhaustion of Berberine inclusion.

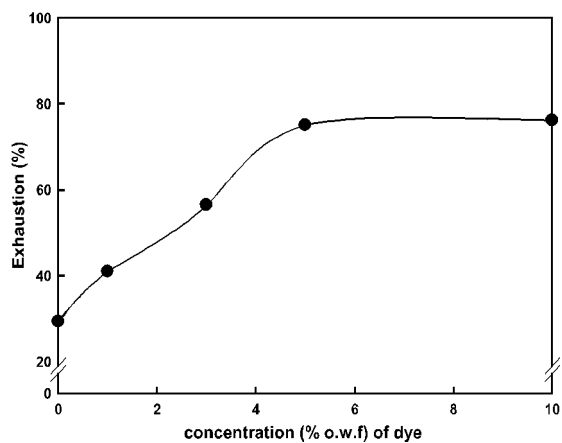


Fig. 6. Effect of dye bridge concentration on the %exhaustion of Berberine inclusion.

4. Conclusions

β -cyclodextrin can be anchored to cellulosic substrates by hetero-bi-functional reactive dye as a role of bridge agent. β -cyclodextrin is capable of forming inclusion complexes with a guest molecule, Berberine. The %exhaustion of β -cyclodextrin increased with increasing the concentration of dye bridge and the corresponding %exhaustion increase of β -cyclodextrin resulted in the increase of Berberine inclusion complex formation.

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References

1. J. S. Yu, F. D. Wei, W. Gao, C. C. Zhao, Thermodynamic study on the effects of β -cyclodextrin inclusion with berberine, *Spectrochimica Acta Part A*, **58**, 249-256(2002).
2. C. L. Yan, Xl. H. Li, Z. L. Xiu, C. Hao, A quantum-mechanical study on the complexation of β -cyclodextrin with quercetin, *THEOCHEM*, **764**, 95-100(2006).
3. T. Shibusawa, J. Okamoto, K. Abe, K. Sakata, Y. Ito, Inclusion of azo disperse dyes by cyclodextrins at dyeing temperature, *Dyes and Pigments*, **36**, 79-91(1998).
4. J. Szejtli, Cyclodextrins in the Textile industry, *Starch/Starke*, **55**, 191-196(2003).
5. Y. Y. Liu, X. D. Fan, Synthesis, properties used controlled release behaviors of hydrogel networks using cyclodextrin as pendant groups, *Biomaterials*, **26**, 3667-6374(2005).
6. P. Savaroni, S. Parlati, R. Buscaino, P. Piccinini, I. Degani, E. Barni, Effects of additives on the dyeing of polyamide fibers. Part 1: β -cyclodextrin, *Dyes and Pigments*, **60**, 223-232 (2004).
7. P. Fini, M. Castagnolo, L. Catucci P. Cosma, A. Agostiano, Inclusion complexes of Rose Bengal and cyclodextrins, *Thermochimica acta*, **15**, 33-38(2004).
8. T. Omura, K. Yologawa, Y. Kayane, Y. Tezuka, Design and properties of reactive dyes with heterobifunctional reactive systems, *Dyes and Pigments*, **29**, 1-21(1995).
9. J. A. Taylor, K. Pasha, D. A. S. Phillips, The dyeing of cotton with hetero bi-functional reactive dyes containing both a monochlorotriazinyl and a chloroacetyl amino reactive group, *Dyes and Pigments*, **51**, 145-152(2001).
10. R. M. El-Shishtawy, Y. A. Youssef, N. S. E. Ahmed, A. A. Mousa, The use of sodium edate in dyeing: II. Union dyeing of cotton/wool blend with hetero bi-functional reactive dyes, *Dyes and Pigments*, **72**, 57-65(2007).