

# Synthesis of Chemically Modified Chitosans with a Higher Fatty Acid Glycidyl and Their Adsorption Abilities for Anionic and Cationic Dyes

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**ABSTRACT:** Novel chitosan-based materials with a higher fatty acid glycidyl as the chemically modified agent were synthesized and the adsorption ability of the resulting polymers has been evaluated for typical anionic and cationic dyes. The successful modification was confirmed by the infrared spectroscopic measurements. As the degree of substitution was decreased, the adsorption ability of the chemically modified chitosans for anionic dyes at the higher dye concentration was increased, and the modified chitosans with a lower degree of substitution showed a higher adsorption ability than that of an activated carbon at the higher dye

concentration. For cationic dyes, the chemically modified chitosan showed a good adsorption power, especially when the adsorption power was evaluated by the flow methods. The improved adsorption ability of a chemically modified chitosan material was also confirmed by comparing it with that of a crosslinked chitosan material. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 2423–2428, 2005

**Key words:** long aliphatic chain; chemically modified chitosan; adsorption; anionic dye; cationic dye

## INTRODUCTION

Chitosan is a polymer of  $\beta$ -1,4-linked 2-amino-2-deoxy-D-glucopyranose derived by N-deacetylation of chitin in an aqueous alkaline solution and is well known to be nontoxic, biocompatible, and biodegradable. Since chitosan (i.e., 100% deacetylated chitin) has three functional groups, two hydroxyl groups and one amino group, per a glucosamine unit, several new functionalities have been produced with the modification of these groups, and the resulting polymer shows a unique character different from that of the parent chitosan molecule.

In our previous work, several chitosan-based adsorbents (crosslinked chitosan) were synthesized by reacting the chitosan with a higher fatty diacid diglycidyl as the crosslinker, and the adsorption characteristics of the crosslinked materials have been investigated for the hydrophilic organic compounds (such as acid dyes) and the hydrophobic compounds (such as 4-Nonylphenol, and dioxins). The results showed that the crosslinked chitosans have excellent adsorption abilities for acid dyes<sup>1</sup> and 4-Nonylphe-

nol,<sup>2</sup> as well as remarkable adsorption ability for dioxins.<sup>2</sup> Taking advantage of the three-dimensional crosslinked structure, the crosslinked chitosan materials was further applied as the stationary phase in high-performance liquid chromatography (HPLC), where an excellent molecular shape planarity recognition power was also confirmed for the separation of polycyclic aromatic hydrocarbons (PAHs).<sup>3</sup>

In this study, novel chitosan-based adsorbents, synthesized by the reaction of chitosan with a higher fatty acid glycidyl, have been introduced as the adsorbent for typical anionic and cationic dyes. The adsorption behavior of four chemically modified chitosans with different degrees of substitution has been systematically studied at various pH values and compared with that obtained by the parent chitosan. As typical anionic dyes, CI Acid Red 1, CI Acid Red 138, CI Acid Orange 7, and CI Acid Red 88 were employed as the anionic sample probes, and two cationic dyes, Methylene Blue and Crystal Violet were also used as the cationic representatives.

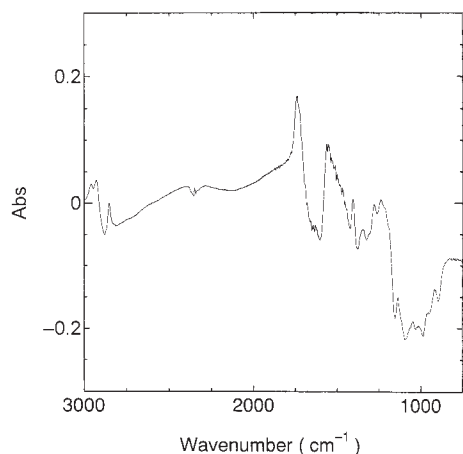
## EXPERIMENTAL

### Materials and reagents

The chitosan (FM80, the degree of N-deacetylation: 85.0%) was provided by Koyo Chemical Co., Osaka,

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**Figure 1** Differential spectrum of IR between OCC-3 and the parent chitosan material.

the sample measured using a Yanaco CHN Corder MT-5 (Yanagimoto Seisakusyo, Co., Tokyo, Japan). Table I shows the results of the elemental analysis of the chemically modified chitosans and the degree of substitution determined from the C/N ratio. The chemically modified chitosans synthesized were termed OCC-1, OCC-2, OCC-3, and OCC-4 according to the order of higher substitution

#### Adsorption of acid dyes and cationic dyes on chemically modified chitosans

A 0.015 g sample of the chemically modified chitosan was added into 200 mL of dye solution at the prescribed pH (it was prepared by using the buffered solution of 0.1 mol/L as the total electrolyte concentration), and the mixture continued to be stirred at 40°C until the equilibrium was established. After the adsorption process, a part of the solution was poured into the test tube and centrifuged for 30 min. The dye concentration of the supernatant liquid was determined by colorimetry measurements at each  $\lambda$  max.

Instead of the batch method, the adsorption of a cationic dye (MB) on OCC-1 and a crosslinked chitosan was measured with a flow method, because the flow method seemed to be more suitable for the kinetic analysis of the adsorption behavior, and, in fact, the

conditions of the flow method measurements are quite similar to those of the real applications as the adsorbent. The crosslinked chitosan was synthesized previously by the reaction of a higher fatty diacid diglycidyl with chitosan, and the degree of substitution for the amino group was determined as 34.8% by the elemental analysis.<sup>2</sup> A column was filled separately with these substrates, and MB solution of pH 8.0 was passed through the column at the average flow rate of 4.65 mL/h. The elute was fractionated separately, and the dye concentration was measured for each fraction. The adsorption percentage was determined with the following equation:

$$\text{Adsorption percentage} = (1 - C_f/C_0) \times 100 \quad (1)$$

where,  $C_0$  is the concentration of an original dye solution and  $C_f$  is the dye concentration of each fraction.

#### Comparison of adsorption velocity of acid dye for chemically modified chitosan and crosslinked chitosan

A 0.015 g sample of the chemically modified chitosan or crosslinked chitosan was added to 200 mL of dye solution of pH 5.0, and the mixture was stirred at 40°C. To determine the adsorption velocity, the mixtures were prepared independently for the measurements at each elapsed time, and a part of the solution was sampled into the test tube and centrifuged for 30 min at room temperature. The dye concentration of the supernatant liquid was determined as mentioned above.

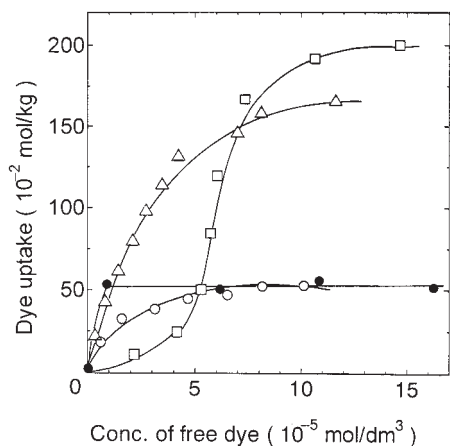
## RESULTS AND DISCUSSION

#### Adsorption of Orange 7 on chemically modified chitosans

The adsorption behavior of Orange 7 on the chemically modified chitosans with different degrees of substitution was studied in the buffer solution of pH 5.0 at the temperature of 40°C. The adsorption isotherms are shown in Figure 2 along with the data on an activated carbon (analytical reagent grade; Nacalai Tesque Inc.,

**TABLE I**  
Results of Elemental Analysis of the Chemically Modified Chitosans and the Degree of Substitution (%)

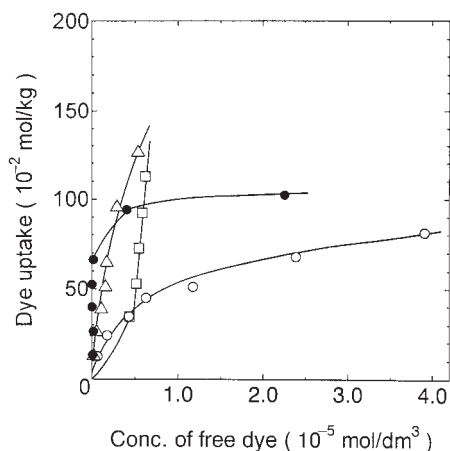
Chemically modified chitosan	H (%)	C (%)	N (%)	C/N	Degree of substitution (%)
OCC-1	8.456	57.813	3.174	18.889	83.9
OCC-2	8.040	50.646	4.304	11.769	41.7
OCC-3	7.477	41.350	4.324	9.563	27.2
OCC-4	7.567	43.799	5.576	7.854	16.0
Original chitosan	7.426	40.906	7.571	5.403	0.0



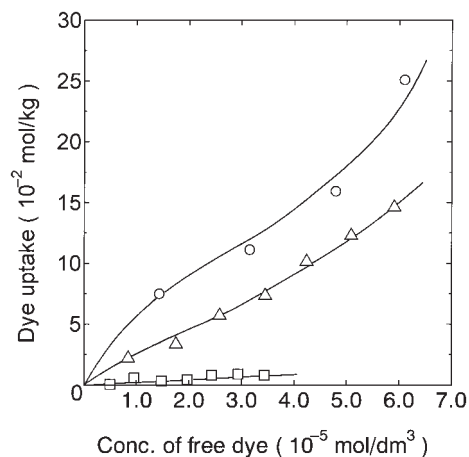
**Figure 2** Adsorption isotherms of CI Acid Orange 7 by the chemically modified chitosans in the buffer solution of pH 5.0 at 40°C. ○: OCC-1; △: OCC-2; □: OCC-3; ●: activated carbon.

Kyoto, Japan) of the same average size. From Figure 2 it can be said that the adsorption ability of chemically modified chitosans at the higher dye concentration decreased in the following order: OCC-3, OCC-2, OCC-1. As the degree of substitution was decreased, the adsorption ability was increased. This is because a typical anionic dye (Orange 7) binds to the protonated amino groups in the substrate. In the lower dye concentration, however, the adsorption ability of OCC-3 is the lowest. The results clearly suggest the presence of the many unreacted amino groups in the substrate as reported previously,<sup>1</sup> where the amino groups are fully hydrated and not uniformly distributed in the substrate.

On the other hand, this phenomenon was not found in the cases of the adsorption of OCC-1 and OCC-2



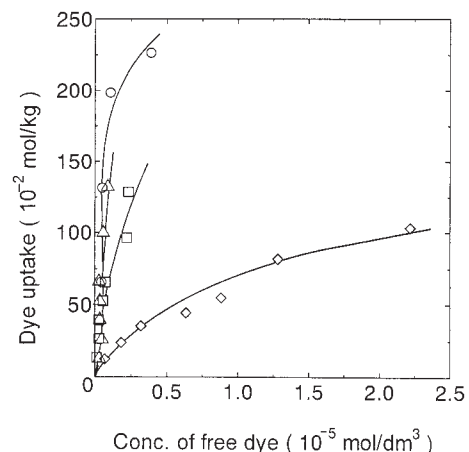
**Figure 3** Adsorption isotherms of CI Acid Red 88 by the chemically modified chitosans in the buffer solution of pH 6.0 at 40°C. ○: OCC-1; △: OCC-2; □: OCC-3; ●: activated carbon.



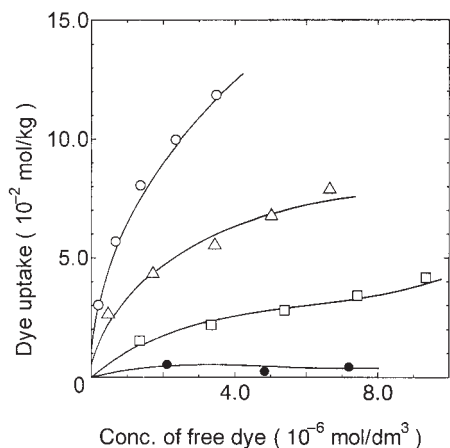
**Figure 4** Effect of pH on the adsorption of CI Acid Red 1 by OCC-3. ○: pH 5.0; △: pH 6.0; □: pH 7.0.

with fewer contents of amino groups. This is estimated because chitosan with a higher degree of deacetylation has more hydrophobic character. The chemically modified chitosans with a lower degree of substitution showed higher adsorption ability than that of an activated carbon at the higher dye concentration.

Next, the adsorption of Red 88 onto three chemically modified chitosans was measured in the buffer solution of pH 6.0 at 40°C. Figure 3 shows the adsorption isotherms. With this dye, it can be also said that the adsorption ability would increase with increase of the content of amino groups in the substrate. However, the trend was not well defined due to the very high hydrophobic property of this dye, since the adsorption occurred by the phenomena of coagulation and/or the stacking caused the easier aggregation<sup>1</sup> in the adsorption for OCC-2 and OCC-3. The adsorption ability of an activated carbon for this dye is also infe-



**Figure 5** Effect of pH on the adsorption of CI Acid Red 138 by OCC-3. ○: pH 5.0; △: pH 6.0; □: pH 7.0; ◇: pH 8.0.



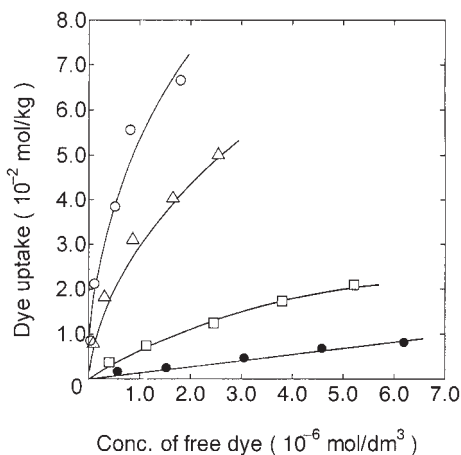
**Figure 6** Adsorption isotherms of Crystal Violet by the chemically modified chitosans and the original chitosan in the buffer solution of pH 8.0 at 40°C. ○: OCC-1; △: OCC-2; □: OCC-4; ●: original chitosan.

rior to those of OCC-2 and OCC-3 at the higher dye concentration.

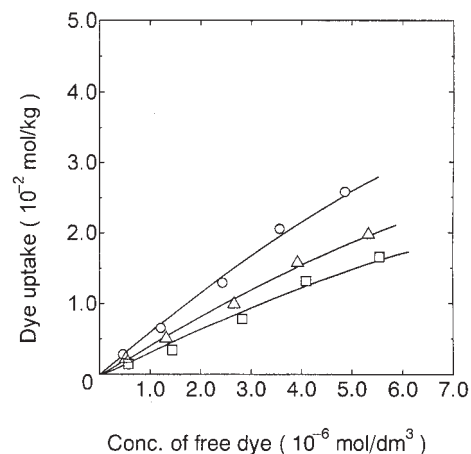
#### Effect of pH on the adsorption of acid dye

The effects of the pH on the adsorption behavior have been investigated for the adsorption of Red 1 and Red 138 onto OCC-3 in the buffer solution of various pH values. The measurement was carried out at 40°C for 72 h. Figures 4 and 5 show the adsorption isotherms obtained for the adsorption of Red 1 and Red 138 onto the substrate, respectively.

The great dependence of the amount of the bound dye on the pH value of the adsorption bath can be seen, because an acid dye binds to the protonated amino groups<sup>4</sup> in the substrate, and the amounts of

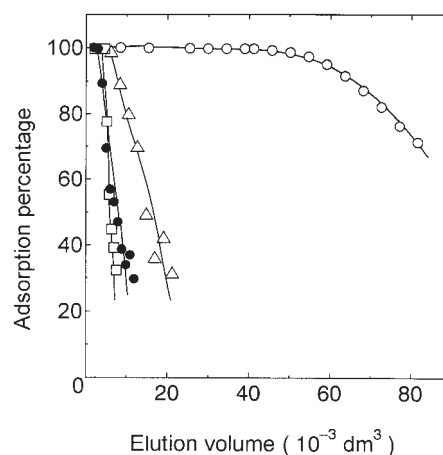


**Figure 7** Adsorption isotherms of Methylene Blue by the chemically modified chitosans and the original chitosan in the buffer solution of pH 8.0 at 40°C. ○: OCC-1; △: OCC-2; □: OCC-4; ●: original chitosan.



**Figure 8** Adsorption isotherms of Methylene Blue by the chemically modified chitosans in the buffer solution of pH 5.0 at 40°C. ○: OCC-1; △: OCC-2; □: OCC-4.

the protonated amino group can increase with the drop in the pH of the bath. Therefore, Red 1 was almost adsorbed on the substrate in the buffer solution of pH 7.0, in which the protonated amino groups are only slightly present in the substrate as shown in Figure 4. On the other hand, the great dependence of the bound dye on the adsorption bath pH is also seen in the adsorption of Red 138. However, the dye was significantly adsorbed in the buffer solution of pH 7.0 and considerably adsorbed even in pH 8.0 (Fig. 5). With Red 1 the ionic bonding between the sulfonic group in the dye molecule and the protonated amino group in the substrate plays exclusively an important role in the adsorption as mentioned above. In contrast, Red 138 is adsorbed via hydrophobic interaction between the alkyl group in the dye molecule and the hydrophobic portion of the substrate, as well as the ionic bonding.<sup>1</sup>



**Figure 9** Relationships between the adsorption percentage and the elution volume. ○: OCC-1; △: crosslinked chitosan; □: cellulose; ●: original chitosan.



### Adsorption of cationic dyes on chemically modified chitosans

The adsorption behavior of MB and CV on the chemically modified chitosans with different degrees of substitution was measured in the buffer solution of pH 8.0 at the temperature of 40°C. The corresponding adsorption isotherms are depicted in Figures 6 and 7 with the data on the original chitosan.

An original chitosan adsorbs CV and MB just a little, whereas the chemically modified chitosans can considerably adsorb those dyes. With a higher degree of substitution, the adsorption amount of both dyes is increased. Figure 8 shows the adsorption isotherms of MB toward the chemically modified chitosans in the buffer solution of pH 5.0. The dye uptake for any of these substrates is much smaller in pH 5.0 than that in pH 8.0. The repulsion between the protonated amino groups in the substrate and the dye cation prevents the adsorption of dye on the substrate in such an acidic pH region. On the other hand the hydrophobic interaction of the hydrophobic part of dye with the aliphatic long chain in the substrate serves the adsorption in the alkaline region without the electrostatic repulsion.

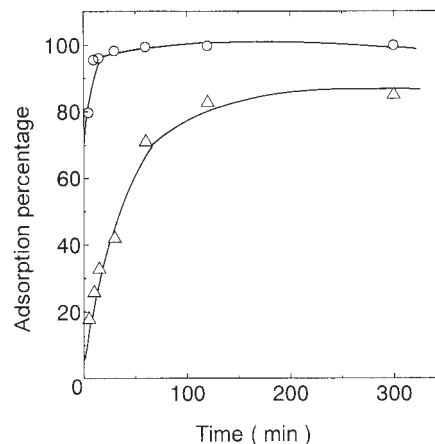
Next the results obtained by the flow method are depicted in Figure 9 with the data on the original chitosan and a cellulose. The adsorption power decreases in the following order:

OCC-1 >> crosslinked chitosan  
> original chitosan  $\cong$  cellulose (2)

The higher adsorption power with OCC-1 results from the introduction of the long aliphatic chains to chitosan. But the lower adsorption power with the crosslinked chitosan is attributed to the low adsorption velocity (as shown in Fig. 10).

### CONCLUSIONS

A novel chitosan-based adsorbent by reacting chitosan with a higher fatty acid glycidyl was synthesized to introduce long aliphatic chains. The adsorption behaviors of several chemically modified chitosans toward



**Figure 10** The amount of adsorption (%) at different adsorption times for the adsorption of CI Acid Orange 7 in the buffer solution of pH 5.0 at 40°C. The amount of adsorption (%) was calculated based on the amount of adsorption at 72 h, at which the establishment of the equilibrium was confirmed. ○ : OCC-3; △ : crosslinked chitosan with degree of substitution of 49.8%.

typical acid dyes and cationic dyes were examined. Their excellent adsorption capabilities for acid dyes and their considerable adsorption power for cationic dyes were demonstrated. Therefore, these chitosan-based materials could be applied as the effective adsorption materials of both anionic and cationic dyes.

Further studies for the adsorption behaviors for hydrophobic organic compounds are currently underway in our laboratory along with applications as novel adsorbent materials for wastewater treatments<sup>2</sup> and a novel stationary phase for the liquid chromatographic separation of complex mixtures.<sup>3,5</sup>

### References

1. Shimizu, Y.; Taga, A.; Yamaoka, H. *Adsorp Sci Technol* 2003, 21, 439.
2. Taga, A.; Nakamura, M.; Shimizu, Y. *Chitin Chitosan Res* 2002, 8, 192.
3. Saito, Y.; Nojiri, M.; Shimizu, Y.; Jinno, K. *J Liq Chromatogr Relat Technol* 2002, 25, 2767.
4. Yoshida, H.; Fukuda, S.; Okamoto, A.; Kataoka, T. *Water Sci Technol* 1991, 23, 1667.
5. Saito, Y.; Nojiri, M.; Shimizu, Y.; Jinno, K. *J Liq Chromatogr Relat Technol* 2004, 27, 275.