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〈研究論文(學術)〉 — 본 연구는 90년도 지방대학 육성연구비의 지원에 의하여 수행되었음 —

# Development of Polymeric Adsorbents for the Treatment of Coloured Waste Waters and it's Application (I)

## — Carboxymethylated Cellulosic Adsorbent System —

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# 有色廢水處理를 위한 高分子吸着制의 開發과 處理水의 再使用 (I)

## — Carboxymethyl화 셀룰로오스흡착제 —

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**요 약**— 셀룰로오스 펄프에 폴리비닐알코올의 블렌드, 가교, 및 카복시메칠화한 아니온성 셀룰로오스계 고분자 흡착제에 대한 모델 카치온 염료, C.I. Basic Red 18의 흡착 및 탈색 성능을 수용액계(pH 4.2)에서 검토하였다. 아니온성 셀룰로오스 고분자 흡착제의 카치온 모델 염료의 흡착등온성은 저농도 영역에서 Sigmoidal 형을 나타내었고 Donnan 흡착 모델 기구로 해석하였다. 하전기 도입에 따라 염료의 흡착능은 증가하였으며 이 흡착능력은 Sodium 이온의 첨가에 의하여 저하하였다. 또 아니온 셀룰로오스계 흡착제에 의한 모델 염료의 배수 탈색율은 크게 증가하였으며 입상활성탄보다 우수한 탈색능력을 나타내었다.

## 1. Introdution

The control of water pollution and reuse of the water recovered from waste-water treatment are one of present mayor target of scientific activity in these days for the protection of environment and the conservation of resources.

The present technology which imparts color fastness and resistance to bleaching, sunlight and oxidation, maker most textile dyes resistant to conventional primary and secondary waste treatment systems.

Also, in addition to their aesthetically unattractive appearance, dye wastes frequently contain metals, such as chromium and copper, that can be toxic not only to aquatic plant and animal life, but also to the microorganisms upon which biological treatment systems rely.

In the present industrial water pollution from dye house has been treated only for the clearance of the waste waters standard and usually treated by combinations of various treatments available today.

Although several methods have been evaluated for treating dye waste streams, the one that appears to be the most feasible is adsorption. The dye waste streams passes through a porous material whose surface attracts the solved dyestuffs in the stream. When the adsorbent is loaded to capacity, it is regenerated to remove the absorbed impurities for disposal in concentrated form and to restore the capacity of the adsorbent.

Granular activated carbon is probably the most common industrial adsorbent and is used to remove color from dye waste streams in some field installations. While producing substantial reduction in color and oxygen demand, activated carbon systems have some limitations.[1]

Mchayet *et al.*[2] reported a mathematical model for the fixed bed adsorption of Telon Blue dye on peat. An adsorption model based on external mass transfer, inesible adsorption, and pore diffusion was developed to predict theorem breakthrough curves for the adsorption of Telon Blue dye from waste water on peat. The curve were effectively correlated to experimental data obtained for a number of design parameters using a single pore diffusivity. The influence of particle size was more difficult to correlate, and the diffusion coefficient varied with pasticle size. This phenomenon may have been due to the inability of the dye to penetrate completely the internal pore structure of the peat particle.

The adsorption behavior of some anionic dyes used in textile industries on newer synthesized adsorbents from guas gum, namely quaternary aminized, and cross-linked derivatives were studied by Kapoor *et al.*[3]

Khare *et al.*[4] discussed the removal of basic dye from waste water using wollastone as sorbent. Batch type experiments indicated that low concentration, small particle size of adsorbent, high temperature, and alkaline pH of the solution are favorable for the removal of crystal violet from aqueous solutions by adsorption on wollastone. The adsoption behavior of the adsorbent follows the langmuir's isotherm. The kinetics of adsorption were studied in the light of adherence of adsorbate molecules on the outer interface of the adsorbent as well as adsorbate transfort within the pores of the adsorbent. The thermodynamics of the process at different temperatures indicate favorable adsorption at the solid-solution interface. Acid-base dissociation of the hydroxylated oxides of the adsorbent and ion exchange with dye cations are the suggested reasons for the maximum removal in an alkaline medium.

In the present work, the properties of sorption and decoloring of a model cation dye, C.I. Basic Red 18 solution by anionically modified carboxymethyl cellulosic adsorbents were investigated to develop the polymeric adsorbents for the treatment of coloured waste waters.

## 2. Experimental

### 2.1 Materials

Cellulose waste pulp (mesh 50~150) and Poly vinylalcohol (DP=1500) as adsorbent material were used.

Dye used for a model waste water was C.I. Basic Red 18 (denoted as Red 18) as a cationic dye.

All chemicals were purchased from Tokyo Kasei Ltd. as standard solution and used without further purification.

### 2.2 Preparation and Characterization of Adsorbents

Cellulosic adsorbents were prepared by mixing and crosslinking of two raw materials selected from cellulose waste pulp and polyvinylalcohol (DP=1500). These adsorbents were conveniently crosslinked to the desired extent by regulating the mole fraction of triacryloyl hexahydro-s-triazine, glutaraldehyde and diammonium hydrophosphate, and were crushed to 150~200 mesh. Carboxylation of crosslinked polymer blends was carried by usual method.[5]

The charge density was determined by back titration method.[6] To determine the acid content of the adsorbent, the adsorbent was immersed in a known amont of standard 0.1 N sodium hydroxide and was back titrated with standard hydrochloric acid using a pH-meter. The characteristics of newly synthesized cellulosic adsorbents are listed in Table 1.

### 2.3 Measurement of adsorption

Equilibrium sorptions were established with a dye solution of pH 4.2 (acetate buffer solution) in glass stoppered Pyrex columns. The temperature was kept constant in a thermostated bath. The amounts of sorbed dye were measured spectrophotometrically by determining the initial and

**Table 1. Adsorbent characteristics**

| Adsorbents | A[a)] | BV[b)] |
|---|---|---|
| $CA_{CM}$-I | 0.07 | 4.21 |
| $CA_{CM}$-II | 0.18 | 3.90 |
| $CA_{CM}$-III | 0.43 | 4.01 |
| $CA_{CM}$-IV | 0.68 | 4.01 |
| $CA_{CM}$-V | 0.84 | 4.24 |

[a)]charge density (m·eq/g), [b)]bed volume (ml/g).

final bath concentrations.

### 2.4 Measurement of decolouring parameter

Flow method using column as fixed bed at ambient temperature was employed. Apparatus employing polymeric adsorption to decolourize streams containing waste dyestuffs consists of columns with 2.0 cm dia. Each column was filled with a known volume of adsorbent, and then pumped independently at flow rates expressed as bed volumn (BV) per hour.

The concentration of treated dye solution was determined spectrophotometrically.

colour removal percent (DD %) $= D_o - D_t/D_o$

where $D_o$ : concentration of dye in waste water
$D_t$ : concentration of dye in treated water
breakthrough point : 90% colour removal point

## 3. Results and discussion

### 3.1 Analysis of sorption isotherms

The sorption isotherms are shown in Fig. 1. This suggests that the amount of sorption is decided solely by carboxy contents of the adsorbents.

The sorption isotherms of Red 18 on partially carboxymethylated rayon fiber were reported as Langmuir type.[7] But as shown in Figures, the shapes of the isotherms obtained in this work are sigmoidal in the lower concentration range and similar to the binding isotherms for other systems.[8]

To interpret the isotherms, Donnan equilibrium mechanism[9] was assumed and interaction parameters were calculated by means of the following equation.

$$\Theta_D = \lambda K_D C_D / \overline{C}_{COOH} \quad (1)$$

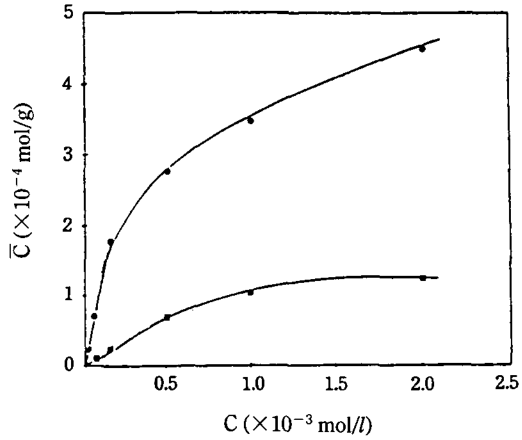


**Fig. 1. Sorption of Red 18 by carboxymethyl polymeric adsorbent in an aqueous solution (pH=4.2) at 25°C.**
■ $CA_{CM}$-II, ○ $CA_{CM}$-III.

where, $\Theta_D$ : the degree of site occupation by dye cation,
i.e. $\theta_D = \overline{C}_D/\overline{C}_{COOH}$
$\overline{C}_{COOH}$ : total acidic sites, mol/kg-dry adsorbent
$K_D$ : the amounts of dye sorbed, mole/kg-dry adsorbent
$C_D$ : the dye concentration of dye in solution, mole/l

The electroneutrality condition in adsorbent leads to equation (2).

$$\lambda(K_D C_D + K_H C_H + K_{Na} C_{Na}) - [K_A \overline{C}_{COOH} / (\lambda K_H C_H + K_A)] = 0 \quad (2)$$

From eq. (1) and eq. (2)

$$\Theta_D = -P_1/2[1-(1+4/P_1P_2)^{1/2}] \quad (3)$$

$$\text{where, } P_1 = K_A K_D C_D / \overline{C}_{COOH} K_H C_H \quad (4)$$

$$\text{and } P_2 = 1 + K_H C_H / K_D C_D + K_{Na} C_{Na} / K_D C_D \quad (5)$$

By plotting the relation between log $\Theta_D$ against log $(C_D/C_H)$ using an observed values of $\overline{C}_{COOH}$, $C_D$ and $C_H$ to reproduce the experimental results, the value of $K_D/K_H$ could be found.

The curve of are shown by a solid line in Fig. 2 and interaction parameter thus obtained are listed in Table 2.

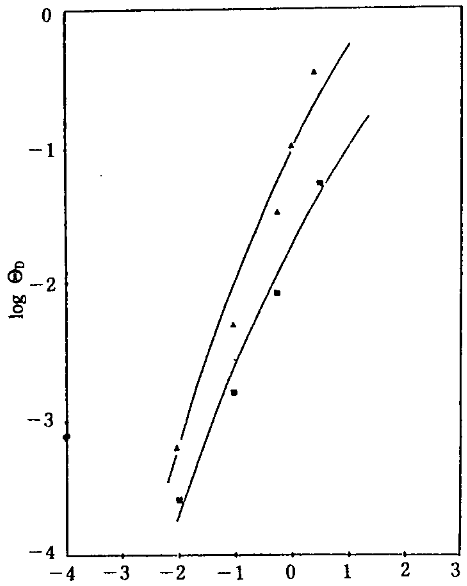


Fig. 2. log $\Theta_D$ vs. log ($C_D/C_H$) at 25°C (▲) and 45°C (■). $CA_{CM}$-III.

Table 2. Distribution coefficient, $K_D/K_H$

| Adsorbents | $K_D/K_H$ | |
|---|---|---|
| | 25℃ | 45℃ |
| $CA_{CM}$-I | 5.0 | 2.0 |
| $CA_{CM}$-II | 11.2 | 4.0 |
| $CA_{CM}$-III | 19.2 | 6.8 |
| $CA_{CM}$-IV | 25.6 | 8.2 |
| $CA_{CM}$-V | 42.2 | 12.6 |

The higher the charge density the larger the distribution coefficient and the higher the temperature the lower the coefficient.

### 3.2 Charge density effect on dye sorption

In order to demonstrate the effect of the charge density on the dye ability, dye uptake contents of the adsorbents equilibrated with solutions of the same concentration were plotted against charge density. Ordinate was taken as a ratio of dye content to charge density.

A part of the charged carboxylated groups acts as a site for the dye cation, and these carboxylated groups are used for electrostatic interaction with the dye cation.

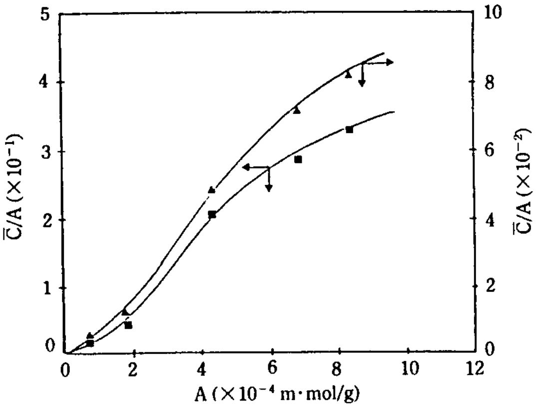


Fig. 3. Charge density effect on equilibrium sorption of Red 18 at 25°C (■) and 45°C (▲) in aqueous solution (pH=4.2).
$C_D=1.0\times10^{-4}$ mol/$l$, $C_{Na}=5.0\times10^{-3}$ mol/$l$.

The increasing tendency with increase of charge density in Fig. 3 is similar to that obtained in other charged cellulosic systems.[10]

### 3.3 Salt effect on dye sorption

Typical results obtained on the influence of sodium ion concentration on the equilibrium dye sorption in case of low dye concentration were in Fig. 4. At high concentration, no remarkable change in dye sorption was observed.

Dye sorption by polymeric adsorbents ($CA_{CM}$-I, $CA_{CM}$-II) decreases with increasing sodium ion concentration in aquese solution. The results indicated that Dye sorption decreases due to the competition of sodium ions with dye cations. This strongly suggests that the main force of attraction between charged carboxyl adsorbent groups and dye cation is electrostatic in nature.[11] The secondary binding force of this system is non-electrostatic interaction such as physical sorption between adsorbent matrix and dyes. This tendency of the change is consistent with the results of Davidson.[12]

### 3.4 Decolouring of a model dye, Red 18 solution

Decolouring effects by cellulosic adsorbents with carboxyl group upto breakthrough point (90% colour removal) for a model cation dye, Red 18 solution were measured at 25℃ by the flow method. Results obtained are shown in Fig. 5.

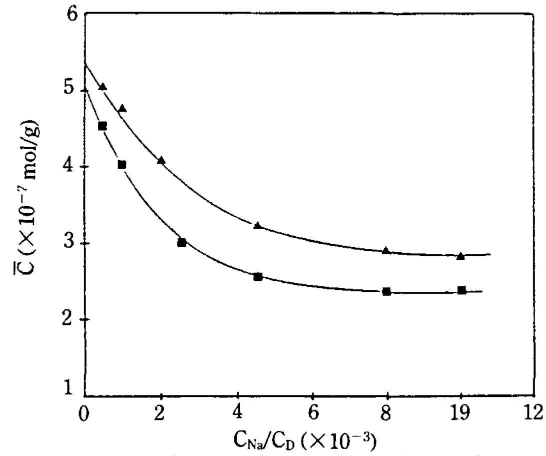


**Fig. 4. Effect of sodium ion concentration on the sorption of Red 18 at 25°C in aqueous solution (pH=4.2).**
$C_D=1.0\times10^{-5}$ mol/*l*, ■ $CA_{CM}$-I, ▲ $CA_{CM}$-II.

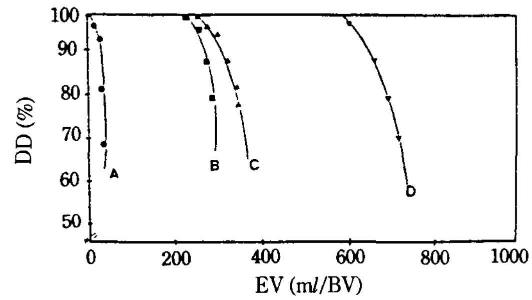


**Fig. 5. Effect of carboxyl group on the decolouring of a model dye, Red 18 solution (pH=4.2) at 25°C.**
Elution velocity A : $CA_{CM}$-I, B : Active carbon (granular), C : $CA_{CM}$-II, D : $CA_{CM}$-IV.

The results have shown that decolouring capacities of cellulosic adsorbents are generally much better than that of granular activated carbon, especially for treating the cationic coloring matter, and that the higher carboxyl group the larger the breakthrough point.

The ionic functionality of polymeric adsorbents is restored by the treatment of adsorbent with dilute acetic acid, and had more 92% efficiency for about 10 cycles.

## 4. Conclusions

Sorption and decolouring phenomena of a model cationic dye, C.I. Basic Red 18 by anionically modifided carboxymethyl cellulosic adsorbents were investigated. The results obtained from sorption experiments were interpreted by Donnan sorption theory.

From the results of this work, following conclusions were obtained.

1) Sorption isotherms of C.I. Basic Red 18 were sigmoidal in low concentration region and suggests strongly that binding involves a Donnan sorption.

2) The higher the charge density the larger the distribution coefficient and the higher the temperature, the smaller the coefficient.

3) The influence of sodium ion on the equilibrium sorption in low dye concentration were found.

4) In the decolouring rate of a model cationic dye, C.I. Basic Red 18, newly synthesized cellulosic adsorbents were generally much better than granular activated carbon.

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