Properties of Carbonaceous Material Produced from Cotton and Its Dye Adsorption Capabilities

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In this study, methylene blue (MB), orange II (ORII), and indigo carmine (IC) were used as adsorbates. Untreated (CT) and treated cotton (CT400, CT600, CT800, and CT1000) were prepared from waste cotton, and their respective physical (i.e., specific surface area, pore volume, and mean pore diameter) and chemical properties (i.e., yield percentage, base consumption, and amount of pH solution added to the adsorbent) were investigated. Scanning electron microscope images of CT, the adsorption rate, and the adsorption isotherm were also analyzed. The specific surface area, pore volume, and mean pore diameter of CT1000 was greater than that of other CT varieties, indicating that the pores on the CT surface were generated by carbonization. Additionally, yield percentage and base consumption decreased because of carbonization. Equilibrium adsorption (i.e., MB, ORII, and IC) was reached within 12 h. The experimental data were fitted to a pseudo-second-order model, suggesting that the adsorption might be a chemisorption process, for which the correlation coefficient, R, equals 1.000. The amount of dye adsorbed onto CT1000 was as follows: IC (290 mg/g) < MB (446 mg/g) ~ ORII (452 mg/g). These experimental data were fitted to the Freundlich equation. The present study implies that the adsorbent for dye removal can be produced from waste cotton and that it is useful for the purification of dye solution systems.

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Keywords: Methylene blue; Orange II; Indigo carmine; Cotton; Carbonaceous material

I. INTRODUCTION

Dye effluent being released into the environment is a major concern. The discharge of dyes is generally from industries that produce textiles, dyestuffs, and so on. There are more than 100,000 types of dyes, with over 700,000 tones of dyestuffs produced annually [1]. These dyes have aromatic molecular structures; this indicates that the biodegradation of these materials is difficult. Moreover, these dyes are directly toxic to microbial populations and can even be toxic and/or carcinogenic to mammals [2]. Therefore, dye removal techniques are being intensely investigated. The various techniques for dye removal that have been reported in the literature include biological treatments, coagulation/flocculation, ozone treatments, chemical oxidation, membrane filtration, ion exchange, photocatalysis, and adsorption [3–10]. Among them, the adsorption technique for dye removal has recently attracted widespread attention [11] and it is one of the most effective methods of dye removal [12]. Adsorption methods using lotus leaves, luffa cylindrical fibers, wood apple shells, activated carbon, zeolite, and fly ash have been evaluated for the removal of dyes [2, 13–17]. However, the widespread utilization of these materials is limited by the cost factor.

On the other hand, 2 million tons of waste textiles (consisting of ~60% of cotton) are exhausted in Japan every year. Of those waste textiles, only ~10% is recycled and reused. The remaining 90% of waste textiles undergoes incineration or is sent to landfills. Cotton is produced from raw cotton, whose main structure is cellulose (D-glucose units are connected via β-(1→4) linkages). If waste cotton were to be used as an adsorbent to remove dyes from aqueous solutions, then such a utilization would solve both the problems mentioned above. First, these waste textiles would be recycled instead of being incinerated or sent to landfills, and second, better wastewater purification would be achieved. Thus, the aim of the current study is to produce an adsorbent from waste cotton and to evaluate its dye adsorption capacity.

II. EXPERIMENTAL

A. Materials

Methylene blue (MB) and Orange II (ORII) were purchased from Wako Pure Chemical Industries Co., Ltd. and Indigo carmine (IC) was purchased from Tokyo Chemical Industries Co., Ltd. The molecular structure of these dyes is shown in Fig. 1. Carbonaceous material from cotton (CT) was prepared according to the following method. First, CT is placed in a muffle furnace and heated to the target temperature (400, 600, 800, and 1000°C, respectively, for CT400, CT600, CT800, and CT1000) for 2 h. The yield percentage of the calcined CT samples was calculated by comparing the weight be-

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Before and after calcination. Scanning electron microscopy (SEM) was conducted on the CT samples using a JSM-5200 (JEOL, Japan). Specific surface area, pore volume, and mean pore diameter were measured by a specific surface analyzer: NOVA4200e (Yuasa Ionic, Japan). The surface functional groups on the CT samples were measured using the method reported by Boehm et al. [18, 19]. The amount of pH solution added to the CT samples was measured by an activated carbon test method (JIS K1474). Element analysis of carbon, hydrogen, and nitrogen was conducted using a MICRO CORDER JM10 (J-SCIENCE LAB Co., Ltd.).

### B. Adsorption rate and adsorption isotherm of MB, ORII, and IC on CT samples

After adding 0.5 g of the CT sample to 500 mL of 100 mg/L dye solution (MB, ORII, and IC), the new solution was shaken at 25°C for a period between 1 min and 48 h. A 3-mL dye solution was collected at the end of the time interval. The dye solution was filtered with a 0.45-µm membrane filter and examined using a UV-1200 (Shimadzu). The amount of dye adsorbed was calculated by comparing the dye concentration before and after adsorption. The adsorption wavelengths used for MB, ORII, and IC were 655 nm, 485 nm, and 612 nm, respectively. The amount of dye adsorbed was calculated by the following equation:

\[
X = (C_0 - C_e)V/W,
\]

where \(X\) is the amount of dye adsorbed (mg/g); \(C_0\) (mg/L), the initial concentration; \(C_e\) (mg/L), the equilibrium concentration; \(V\) (L), the solvent volume; and \(W\) (mg), the weight of the CT sample. The adsorption isotherm of the dye on CT1000 was obtained by the following procedure: After adding 0.05 g of CT1000 to 50 mL of dye solution at different initial concentrations, the new solution was shaken at 25°C for 48 h at 100 rpm. The concentration of the dye filtered with a 0.45-µm membrane filter was measured using a UV-1200 (Shimadzu), and the amount of dye adsorbed onto CT1000 was calculated using Eq. (1). From these experiments, we confirmed that untreated cotton (CT) had no dye adsorption capability.

### III. RESULTS AND DISCUSSION

#### A. Properties of the CT samples

The specific surface area, pore volume, and mean pore diameter of the CT samples are listed in Table I. As can be seen in Table I, the specific surface area of CT increased with an increase in the temperature of calcination. The specific surface area of CT1000 (1253 m²/g) was greater than that of every other CT variety. The micro pore volume (0.161 mL/g) and meso pore volume (0.152 mL/g) of CT1000 also increased with an increase in the calcination temperature, indicating that the specific surface area depends on the generation of micro and meso pore volumes in the CT sample. In general, pore volume was separated, respectively, by micro pore (5 < \(d\) ≤ 20 Å), meso pore (20 < \(d\) ≤ 500 Å), and macro pore (\(d\) > 500 Å) regimes [20]. The generation of pore volume appears to have a larger effect on dye adsorption. Carbonaceous material from CT demonstrated a similar trend. Further, the mean pore diameter of CT1000 is larger than those of the other CT varieties.

The yield percentage, base consumption, and amount of pH solution added to the CT samples are listed in Table II. From Table II, one can see that the yield percentage of CT decreased with an increase in the calcination temperature. Also, the yield percentage of CT1000 (7.4%) was smaller than that of the other CT varieties, indicating that carbonization occurred. The base consumption values demonstrate that there are a number of acidic functional groups (e.g., carboxyl, phenolic, and lactonic) present on the CT surface. Overall, the base consumption of CT was decreased by increasing the calcination temperature. Hydroxyl groups from the cellulose structure were also present on the CT surface. However, these functional groups likely disappeared with carbonization. The amount of pH solution added to the CT samples shifted the basic conditions with the increase in the

![Table I: Physical properties of CTs.](image)

| Sample | Specific surface area (m²/g) | Pore volume (mL/g) | Mean pore diameter (Å) |
|--------|-----------------------------|-------------------|----------------------|
| CT     | 0                           | 0.000             | —                    |
| CT400  | 186                         | 0.001             | 0.270                |
| CT600  | 381                         | 0.009             | 1.346                |
| CT800  | 564                         | 0.026             | 4.113                |
| CT1000 | 1253                        | 0.161             | 10.198               |

![Table II: Chemical properties of CTs.](image)

| Sample | Yield percentage (%) | Base consumptions (mmol/g) | pH  |
|--------|----------------------|----------------------------|-----|
| CT     | —                    | 0.45                       | 6.6 |
| CT400  | 24.1                 | 2.65                       | 5.2 |
| CT600  | 15.5                 | 0.96                       | 7.5 |
| CT800  | 10.2                 | 0.95                       | 8.0 |
| CT1000 | 7.4                  | 0.73                       | 8.5 |
Concentration of dyes (mg/L)
Amount adsorbed (mg/g)

The amount of adsorbed material was in the following order: CT400 < CT600 < CT800 < CT1000. The equilibrium adsorption of the dye was reached within 12 h. Adsorption kinetics are of critical importance to the design of practical treatment systems, and hence, pseudo-first-order and pseudo-second-order equations were tested to fit the experimental data. Kinetic models have been proposed to elucidate the mechanism of adsorption, which depends on the physical and/or chemical characteristics of the adsorbent as well as the mass transport process [21]. The pseudo-first-order equation is the most commonly used equation to describe adsorption, and it is determined by the following equation:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

where \( q_t \) (mg/g) is the amount of dye adsorbed at time \( t \) (h); \( q_e \) (mg/g), the equilibrium adsorption; and \( k_1 \) (h\(^{-1}\)), the rate constant of the pseudo-first-order model [22].

The pseudo-second-order model can be expressed as follows:

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{t}{q_e},$$

where \( k_2 \) (mg/g/h) is the rate constant of the pseudo-second-order model [23]. The constants that were calculated are given in Table III. The correlation coefficients (MB, ORII, and IC) for the pseudo-first-order model and pseudo-second-order model were 0.963-1.000 and 1.000, respectively. Constants \( k_1 \) and \( k_2 \) for MB, ORII, and IC were 128.42 and 2.64, 122.16 and 27.25, and 14.20 h\(^{-1}\) and 0.69 mg/g/h, respectively. These experimental data fit more closely with the pseudo-second-order model, indicating that the adsorption mechanism of the dye onto the CT was chemisorption [24].

C. Adsorption isotherm

The adsorption isotherm of the dye onto CT1000 is shown in Fig. 4. As seen in the figure, the amount of dye adsorbed followed the trend: MB \( \approx \) ORII > IC. The amount of MB and ORII adsorbed onto CT1000 was greater than that of IC adsorbed onto CT1000. Adsorption isotherms are important for revealing the adsorption mechanism for the interaction of the adsorbate with the adsorbent. The dynamic adsorptive separation of the solute from the solution onto an adsorbent depends on the accuracy of the description of the equilibrium separation that occurs between the two phases [25]. Many models have been proposed to describe the adsorption process; the Langmuir and Freundlich isotherm models are the

FIG. 3: Adsorption rate of dyes onto CTs.

FIG. 4: Adsorption isotherms of dyes onto CT1000.
TABLE III: Kinetic parameters for dyes adsorption onto CT1000.

| Dye                | Pseudo-first-order model | Pseudo-second-order model |
|--------------------|--------------------------|---------------------------|
|                    | $q_e$ (mg/g)             | $k_1$ (h$^{-1}$)          | $R$                        |
| Methylene blue     | 100.0                    | 128.42                    | 1.000                      |
| Orange II          | 99.9                     | 122.16                    | 0.996                      |
| Indigo carmine     | 98.7                     | 14.20                     | 0.963                      |

| Dye                | $q_e$ (mg/g)             | $k_2$ (mg/g/h)            | $R$                        |
|--------------------|--------------------------|---------------------------|---------------------------|
| Methylene blue     | 100.0                    | 2.64                      | 1.000                      |
| Orange II          | 100.0                    | 27.25                     | 1.000                      |
| Indigo carmine     | 99.9                     | 0.69                      | 1.000                      |

TABLE IV: Freundlich and Langmuir constants for dyes adsorption onto CT1000.

| Dye                | Freundlich constant | Langmuir constant |
|--------------------|---------------------|-------------------|
|                    | $1/n$               | $\log K$          | $a$ (L/mg)         | $W_s$ (mg/g) | $R$          |
| Methylene blue     | 0.03                | 2.60              | 1.42              | 449.4       | 0.915        |
| Orange II          | 0.07                | 2.55              | 0.73              | 468.0       | 0.972        |
| Indigo carmine     | 0.19                | 1.99              | 0.25              | 235.4       | 0.858        |

most commonly used ones [26, 27]. The Langmuir adsorption isotherm model assumes that adsorption takes place at specific homogeneous sites within the adsorbent and that there is a uniform distribution of energetic adsorption sites. As a consequence, once an adsorbate molecule occupies a site, no more adsorption can take place. Therefore, Langmuir’s model is only valid for monolayer adsorption onto a surface with a finite number of identical sites. Langmuir parameters are determined according to the following equation:

$$q = aW_sC_e/(1 + aW_s),$$

where $q$ (mg/g) is the amount of dye adsorbed; $a$ (L/mg), a constant related to the affinity to the binding sites and of the adsorption; $W_s$ (mg/g), the maximum monolayer adsorption capacity; and $C_e$ (mg/L), the equilibrium concentration.

Langmuir constants for the adsorption of dyes onto CT1000 are listed in Table IV. From Table IV, the Langmuir constant $a$, for MB, ORII, and IC, took the values 1.42, 0.73, and 0.25 L/mg, respectively. The correlation coefficient for MB, ORII, and IC took the values 0.915, 0.972, and 0.858, respectively. The experimental data for ORII most closely adhered to the Langmuir model. Moreover, the amount of dye adsorbed depends on the specific surface area and pore volume (especially, micro and meso pore volumes). The specific surface area and pore volumes of CT1000 were greater than that of every other CT variety. The schematic drawing of dye adsorption onto CT1000 or CT600 is shown in Fig. 5. It is important for dye removal to development of micro and meso pore volume onto adsorbent surface.

Adsorption mechanism of dye onto CT1000 was interaction between the surface functional groups onto CT1000 and the functional groups of dye molecular. Diameter of MB, ORII, and IC were 14.47, 13.26, and 15.95 Å, respectively. Moreover, $N^+$ and $SO_3^−$ are existed in molecular structure of MB and ORII or IC, respectively (refer to Fig. 1). The surface functional groups of CT1000 were thought to be negative charges, therefore, the amount of IC adsorbed onto CT1000 was smaller than that of MB or ORII adsorbed onto CT1000. However, changes of molecular size or electrification for aggregation of dyes and pH condition in aqueous solution systems, which affected the dye adsorption capacity of CT1000.

A comparison of the maximum adsorption capacity of...
TABLE V: Comparison of the maximum adsorption capacity of dye onto various adsorbents.

| Dye             | Adsorbent              | Adsorption capacity (mg/g) | References |
|-----------------|------------------------|----------------------------|------------|
| Methylene blue  | Lotus leaf             | 250                        | [15]       |
|                 | Luffa cylindrical fiber| 50                         | [16]       |
|                 | Wood apple shell       | 95                         | [17]       |
|                 | Spherical chitosan resin| 625                        | [29]       |
|                 | Magnetic beads         | 29                         | [30]       |
|                 | CT1000                 | 446                        | This work  |
| Orange II       | Zeolite                | 3                          | [2]        |
|                 | Activated carbon       | 197                        | [13]       |
|                 | CT1000                 | 452                        | This work  |
| Indigo carmine  | Fly ash                | 2                          | [14]       |
|                 | Silk                   | 5                          | [31]       |
|                 | CT1000                 | 290                        | This work  |

Dyes onto various adsorbents is given in Table V. From Table V, it is clear that CT1000 has a relatively large adsorption capacity with reference to other data published in the literature. The results of our analysis indicate that CT1000 is useful for the removal of dyes from aqueous solution systems [2, 13–17, 29–31].

IV. CONCLUSIONS

Carbonaceous material (CT1000) was prepared from waste cotton. The specific surface area and pore volume of CT1000 was greater than that of the other CT samples. Additionally, the yield percentage and base consumption values for CT1000 were smaller than those of the other CT samples. These results show that carbonization took place in the case of the CT samples. The SEM images of CT did not show visible changes with carbonization. The adsorption rate of the dye was reached within 12 h, and the amount of dye adsorbed was in the following order: CT400 < CT600 < CT800 < CT1000. Moreover, the experimental data was fitted to the pseudo-second-order model (with a correlation coefficient, \( R^2 \), equal to 1.000). The amount of dye adsorbed onto CT1000 was IC (290 mg/g) < MB (446 mg/g) = ORII (452 mg/g). These results fit with the Freundlich model. The conducted adsorption experiments indicate that CT1000 is a very efficient adsorbent for the removal of dye from aqueous solutions.

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