Interactions of Cationic and Anionic Dyes with Activated Carbons

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Five kinds of activated carbon (AC1, AC2, AC3, AC4, and AC5) were prepared, and the characteristics (scanning electron microscopy images, specific surface area, pore-volume, pH_{pzc}, surface functional groups, and surface hydroxyl groups) of each activated carbon were investigated. Additionally, the adsorption capability of activated carbons and adsorption mechanisms involved in adsorption of cationic and anionic dyes from the aqueous solution were evaluated. The results suggested that the treatment of activated carbon with silver (AC3), titanium oxide (AC4), or magnetic field (AC5) was not useful for increasing specific surface area and micropore volume. Moreover, the amount of cationic and anionic dyes adsorbed using activated carbon prepared from coconut shells (AC1 and AC2) were higher than that adsorbed using AC3, AC4, and AC5. Subsequently, the adsorption mechanism involved in adsorption of cationic and anionic dyes was also assessed. It was found that the amount of cationic and anionic dyes adsorbed was related to the specific surface area, micropore volume, and acidic or basic functional groups. Finally, the interactions between dyes and AC1 were elucidated in this study. Adsorption of dyes onto the AC1 surface was confirmed by the elemental distribution and X-ray photoelectron spectroscopy analysis. These results provide useful information on the surface interactions between the activated carbon and dyes (high molecular organic compounds).

**Keywords** Activated carbon; Cationic dye; Anionic dye; Adsorption

I. INTRODUCTION

Dyes are widely used in industries such as textile manufacturing, paper, and pharmaceutical industries [1]. According to the literature, more than 700000 tons of dyes are produced worldwide every year [2]. A large number of dyes are toxic and difficult to degrade by microorganisms when discharged into the water environment. Additionally, the presence of dyes in the aqueous phase largely affects water visibility and transparency, resulting in a reduction of light penetration and oxygen gas solubility in the water phase [3]. Moreover, dyes can impart toxicity to the aquatic organisms and may lead to mutagenic effects in human beings or cause severe damage to organs such as the brain, kidney, liver, and central nervous system [4–6]. Therefore, it is important to remove these harmful dyes from the aqueous phase.

Dyes can be classified into cationic dyes (carrying a positive charge) and anionic dyes (carrying a negative charge) from a chemical standpoint [7]. Previous studies have reported different techniques for the removal of some specific dyes from the aqueous solution [8]. However, it is expected that different types of dyes have different physicochemical properties in the solution. Therefore, it is necessary to evaluate the information on dyes, which were not previously reported, to prevent its toxic effects on aquatic and human life.

Adsorption is considered a promising treatment because...
of its advantages, such as lower cost, simple design and operation, and efficient removal [9]. Studies involving the decolorization of dye wastewater using activated carbon have been previously reported [9, 10]. Activated carbon, which has a high degree of porosity and an extensive surface area, has been a material of choice for adsorption of various pollutants such as organic chemicals, chlorine, lead, and unpleasant tastes or odors. [10–12]. Additionally, adsorption capacity of activated carbon is determined not only by its texture but also by its chemical characteristics, such as surface functional groups [10, 13]. Recently, a large number of studies have evaluated the adsorption capabilities of natural and modified activated carbons under different conditions for the adsorption of various dyes [10, 14]. Many researchers have focused on understanding the surface characteristics of activated carbons, and the relationship between the dye adsorption capability and physicochemical characteristics of activated carbon in detail [1, 9, 11]. However, different types of activated carbon certainly have different capabilities for adsorption of dyes from aqueous solutions [14]. In addition, there are very few reports assessing the correlation between dye adsorption and physicochemical characteristics of activated carbons by the elemental distribution or binding energy analysis.

Therefore, this study aims to understand the interactions between different classes of dyes and physicochemical properties of natural and modified activated carbons. Cationic dye (Kayacryl Light Blue 4GSL-ED) and anionic dye (Kayanol Milling Red BW) were purchased from Shinko Co. Physicochemical characteristics of the activated carbons were measured by the following methods. Scanning electron microscopy (SEM) image was analyzed by SU1510 (Hitachi Ltd.). The specific surface area and pore volume were measured using NOVA4200e (Yuasa Ionics). Surface functional groups, surface hydroxyl groups, and pH<sub>pzc</sub> were measured by Boehm’s titration method [15], adsorption method for fluoride [16], and Faria’s titration method [10], respectively.

II. EXPERIMENTAL

A. Materials and characterization

Five kinds of activated carbon (AC1, AC2, AC3, AC4, and AC5) were procured from Ueda Environmental Solutions (UES) Co., Ltd. Briefly, AC1 and AC2 were highly activated coconut shell-based carbons of high purity. AC3 was characterized by silver nanoparticles impregnated into high-quality coconut shell activated carbon. AC4 was characterized by titanium oxide integrated into coconut shell activated carbon. AC5 was activated carbon having magnetic properties. Cationic blue (Kayacryl Light Blue 4GSL-ED, CAS No. 12221-43-1) and anionic red (Kayanol Milling Red BW, CAS No. 15792-43-5) were purchased from Shinko Co.

B. Determination of adsorption capability of activated carbons

Each activated carbon (0.05 g) was mixed with a 50-mL cationic blue or anionic red solution of 100 mg L<sup>-1</sup>. The reaction solution was subjected to shaking conditions of 100 rpm at 25°C for 24 h. After that, the sample was filtered through a 0.45 µm membrane filter, and the filtrate was analyzed using a spectrophotometer (UV-1200, Shimadzu Co., Ltd.). The amount of dye adsorbed was calculated based on the difference between the dye levels before and after adsorption. Preliminary experiments were carried out to determine the adsorption wavelength and the range for preparing the calibration curve. The absorption wavelengths used for cationic blue and anionic red were 657 and 517 nm, respectively. The calibration curve was prepared over the range of 1–100 mg L<sup>-1</sup> and the correlation coefficient was

Figure 1: SEM images of ACs.
determined to be over 0.999. Additionally, the elemental distribution and X-ray photoelectron spectroscopy (XPS) analysis for elucidating the relationship between the activated carbon adsorption of dyes and physicochemical characteristics of activated carbons were carried out using JXA-8530F (JEOL) under an accelerating of 15.0 kV, prove current of 20 mA, and a beam diameter of 5 μm and AXIS-NOVA (Shimadzu, Co., Ltd.) under an accelerating voltage of 15.0 kV and electric current of 10 mA, respectively.

III. RESULTS AND DISCUSSION

A. Characteristics of activated carbons

SEM images of each activated carbon are shown in Figure 1. The particle size of each activated carbon was in the range 500 μm ≤ r < 1700 μm (r represents radius). It was observed that AC1 and AC2 has a concave-convex surface. There are a large number of small pores in AC3, suggesting that its surface characteristics depend on the treatment process followed for surface activation. No major difference was observed between AC4 and AC5. The physicochemical characteristics of activated carbons are shown in Tables 1 and 2. Specific surface area and micropore volume (d ≤ 20 Å, d represents diameter) of AC1 (978 m² g⁻¹ and 0.0013 mL g⁻¹) and AC2 (1120 m² g⁻¹ and 0.0018 mL g⁻¹) were greater than those of other ACs. Micropores and specific surface area are the major factors determining the adsorbent capability of adsorbate removal from the aqueous phase [17]. Therefore, treatment for surface activation of carbon using silver nanoparticles, titanium oxide, or magnetic field was not useful for increasing the specific surface area and micropores. Moreover, transport within the micropores can be severely limited by the steric effect [17]. These results suggested that the adsorption of dyes onto AC1 or AC2 is higher compared to other activated carbons. There was not much difference in pHₚₑₚ among the activated carbons. Furthermore, the total surface functional groups (the sum of basic and acid functional groups) of AC1 and AC2 were also greater than those of other activated carbons. The value of surface hydroxyl groups was in the order AC1 (0.242 mmol g⁻¹) < AC4 (0.566 mmol g⁻¹) < AC3 (0.724 mmol g⁻¹) < AC2 (0.826 mmol g⁻¹) < AC5 (0.847 mmol g⁻¹). However, this trend was not similar to the trend observed for surface functional groups. In this study, only thecapability of activated carbons in the removal of cationic and anionic dyes from the aqueous phase was evaluated. The mechanism of surface activation of carbon with silver nanoparticles, titanium oxide, or magnetic field was not elucidated in detail. Therefore, further studies are necessary to understand the activation mechanism in detail.

B. Adsorption capability of activated carbons

The amount of dyes adsorbed on the activated carbons is shown in Figure 2. The amount of dyes adsorbed by the activated carbons was in the order AC5 < AC4 < AC3 < AC2 < AC1. The amount of cationic blue adsorbed was higher than that of anionic red because of two major reasons. The size of the cationic blue molecule is smaller than that of the anionic red molecule. Therefore, the quantity of cationic dye adsorbed was greater than that of anionic dye under the same experimental conditions. A similar trend was also reported in previous studies [7, 10, 14]. Subsequently, the correlation between the amount of dyes adsorbed and physicochemical characteristics is shown in Table 3. For the cationic blue, the correlation coefficients

| Sample | Specific surface area (m² g⁻¹) | Pore volume (mL g⁻¹) |
|--------|-------------------------------|---------------------|
|        | d ≤ 20 Å                      | 20 < d ≤ 500 Å      | 500 Å < d | Total |
| AC1    | 978                           | 0.0013              | 0.0336    | 0.0001 | 0.0350 |
| AC2    | 1120                          | 0.0018              | 0.0509    | 0.0004 | 0.0531 |
| AC3    | 870                           | 0.0010              | 0.0350    | 0       | 0.0360 |
| AC4    | 845                           | 0.0009              | 0.0181    | 0       | 0.0190 |
| AC5    | 9                             | 0.0002              | 0.0265    | 0.0053 | 0.0320 |

| Sample | pHₚₑₚ | Surface functional group (mmol g⁻¹) | Surface OH group (mmol g⁻¹) |
|--------|-------|-----------------------------------|-----------------------------|
|        |       | Basic                             | Acid                        |
| AC1    | 7.46  | 0.062                             | 0.077                        | 0.242                        |
| AC2    | 8.20  | 0.077                             | 0.080                        | 0.826                        |
| AC3    | 7.04  | 0.030                             | 0.088                        | 0.724                        |
| AC4    | 7.39  | 0.045                             | 0.077                        | 0.566                        |
| AC5    | 7.16  | 0       | 0.040                        | 0.847                        |

Table 1: Physical properties of ACs.

Table 2: Chemical properties of ACs.
between the amount adsorbed and specific surface area and between the amount adsorbed and micropores was 0.902 and 0.920, respectively. Moreover, the correlation coefficient between the amount of dye adsorbed and acidic surface functional groups was 0.835. Previous studies reported that the mechanism of adsorption of dyes from the aqueous phase using activated carbon was controlled by many factors. These factors were dependent on the physicochemical characteristics such as specific surface area, pore-volume, and surface functional groups of activated carbons and the properties of dyes in the solution [7]. In particular, the adsorption is mainly due to the electrostatic attraction (coulombic attraction) between the charged dye molecules and activated carbon in the solution. Thus, it can be stated that there were potential interactions between cationic blue and activated carbon in this case [9, 18].

For anionic red also, a trend similar to cationic blue was observed. The correlation coefficient between the amount adsorbed and specific surface area was 0.776, and that between amount adsorbed and micropores was 0.828. Additionally, the correlation coefficient between the amount adsorbed and basic surface functional groups was 0.811. However, no significant correlation could be established between the amount of dyes adsorbed and other characteristics of activated carbons. However, various other factors also affect the adsorption capability of dyes in the aqueous solution. Therefore, further studies on the removal of cationic blue and anionic red need to be carried out with a specific focus on the effect of pH, temperature, and contact time on the adsorption capability of activated carbons having different characteristics.

Further, AC1 was selected for elucidating the adsorption mechanisms of dyes in this study because the adsorption capability of AC1 was higher compared to other activated carbons. SEM images of AC1 before and after adsorption of cationic blue and anionic red are shown in Figure 3. It can be implied from Figure 3 that the cationic or anionic dyes were adsorbed onto the AC1 surface. Therefore, the study further demonstrated the interaction between each dye and AC1 adsorbent surface in detail. Figure 4 shows the elemental distribution analysis of the AC1 surface before and after adsorption. Molecular formulae of cationic blue and anionic red are C_{22}H_{22}N_{3}O and C_{30}H_{27}N_{3}O_{8}S_{2}, respectively. The intensity of carbon (C) clearly increased after adsorption in the case of both the dyes. In addition, the intensities (the abundance ratios) of nitrogen (N) and sulfur (S) increased after adsorption were 0.9 % and 0.1 %, respectively. Subsequently, the XPS spectra of N and S on the AC1 surface before and after adsorption were measured (Figure 5). Although no XPS spectrum bears the N 1s and S 2p peaks before adsorption, the N and S related peaks were observed after adsorption.
IV. CONCLUSION

In this study, the adsorption kinetics of cationic blue and anionic red using different activated carbons were elucidated. The amounts of cationic blue and anionic red adsorbed were correlated to the specific surface area ($R = 0.902$ and 0.776), micropore volume ($R = 0.920$ and 0.828), and acidic or basic functional groups ($R = 0.835$ and 0.811). The study indicated that the adsorbent surface characteristics governed adsorption of dyes from the aqueous solution. Adsorption of cationic blue and anionic red onto the adsorbent surface was confirmed from the SEM images, elemental distribution, and the XPS analysis after dye adsorption. Thus, this study highlighted the adsorption mechanism for the removal of cationic and anionic dyes using activated carbon.

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