Decolorization of Acidic Dye by Charcoal from Coffee Grounds

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From the viewpoints of decreasing environmental burdens and recycling of materials, the adsorption ability of charcoal from coffee grounds for acidic dye (acid orange 7) removal was investigated by the batch method. Differences in the removal ratio and removal rate of acid orange 7 could be explained by differences in the properties of charcoal such as specific surface area and pore volume. In the relationship between the amount of acid orange 7 adsorbed at each elapsed time and the square root of elapsed time, a good linearity was recognized. Since the good linearity between the acid orange 7 adsorption and the square root of elapsed time was recognized, the intraparticle diffusion of acid orange 7 onto pores of adsorbents was identified as the rate-limiting step in the adsorption process.

Key words —— coffee grounds, charcoal, acid orange 7, adsorption characteristics, intraparticle diffusion

INTRODUCTION

Wastewater from the dyeing industry contains various contaminants such as starch, color, acid, base and other substances. Among these, color is considered to be the most obvious indicator of water pollution. In addition, wastewaters from dyeing and textile industries more easily form detrimental trihalomethanes after chlorination of the water compared with those from wastewater of other industries.[1] Trihalomethanes are thought to be carcinogenic when ingested by animals.[2,3] Wastewater from the dyeing industry is thought to be one of the important sources of trihalomethane formation.

Various treatments have been carried out for the removal of dye by chemical coagulation,[4] ozonation[5,6] and adsorption.[7,8] Activated carbon is widely used due to its effectiveness and versatility, but this method is expensive. In recent years, low-cost adsorbents have been produced from by-products and their utilization for wastewater treatment has been attempted.[9–12]

Coffee grounds are considered a food waste. Part of the waste is used as a fertilizer, but most of the coffee grounds are dumped or burned. However, coffee grounds are carbonaceous and have the potential to be converted into an adsorbent. This conversion could contribute to reducing the volume of waste, while producing an adsorbent with a lower cost. Moreover, conversion may prevent the discharge of carbon dioxide, one of the causes of global warming.

In this study, we aimed to demonstrate the adsorption characteristics of charcoal from coffee grounds to remove acid orange 7 as one of the acidic dyes for effective utilization of food wastes.

MATERIALS AND METHODS

Materials —— Acid orange 7 was of reagent grade quality (Wako Pure Chemical Co., Ltd., Japan) and used without further purification.

Charcoal from coffee grounds used as an adsorbent was supplied from TORASUTO21 Co. Ltd. (Japan). Charcoals were manufactured as followed; the extracted residue of coffee beans were dried until water content was reduced by 50%, then carbonized in a furnace at 800, 1000 and 1200°C, respectively. Adsorbent particles were sieved through a 10–20 mesh. Before use, adsorbents were washed with distilled water until no fine carbon particles were observed, then dried at 110°C for 48 hr, and stored in a desiccator.

Equilibrium Adsorption —— The equilibrium amounts of acid orange 7 adsorbed onto charcoal were measured by the batch method. A measured amount of adsorbent (0.05, 0.1 and 0.2 g) was added to 30 ml of acid orange 7 solutions (initial concentrations: *ca.* 50, 100, 200, 500 and 1000 mg/l) and shaken at 25°C for 20 days with a shaker bath (ML-10F, TAITEC Co., Japan). After standing, unadsorbed acid orange 7 in the supernatant solution was measured at 485 nm with a spectrophotometer (UV-1200, Shimadzu, Japan). Then the equilib-

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rium amount adsorbed at the equilibrium concentration was calculated by following equation:

$$V = (C_0 - C_\infty) \times 30/(1000 \times W)$$

where V (mg/g) is the amount adsorbed per unit mass of adsorbent, C_0 (mg/l) is the initial concentration, C_∞ (mg/l) is the equilibrium concentration and W (g) is the weight of the charcoal.

Removal Ratio of Acid Orange 7 —— The removal ratios of acid orange 7 by charcoals were measured by the batch method. A measured amount of adsorbent (0.05, 0.1 and 0.5 g) was added to 30 ml of acid orange 7 solution (initial concentration: 10 mg/l) and shaken at 25°C for 20 days with a shaker bath (ML-10F, TAITEC Co.). After standing, unadsorbed acid orange 7 in the supernatant solution was measured. Then the removal ratio was calculated by the following equation:

Removal ratio (%) = $[(C_0 - C_\infty)/C_0] \times 100$

where C_0 is the initial concentration and C_∞ is the equilibrium concentration.

Time Courses of Acid Orange 7 —— The time courses of acid orange 7 adsorption were measured in acid orange 7 solution / adsorbent system at 25°C. Three gram of adsorbent was added to acid orange 7 solution of 300 ml (initial concentration: 10 mg/l) and stirred (200 rpm). Five milliliter of the suspension was taken up at regular intervals and used to measure the acid orange 7 concentrations by spectrophotometry.

Specific Surface Area and Pore Volume —— The specific surface area and the pore volume of charcoals were measured using a Brunauer, Emmett and Teller (BET) apparatus (NOVA1000, YUASA-IONICS Co., Ltd., Japan) with nitrogen gas at liquid nitrogen temperature. The mean pore diameter was calculated using the equation 4 Vp/S, where Vp is the pore volume and S is the specific surface area.

RESULTS

The properties of charcoal from coffee grounds are indicated in Table 1. The specific surface area and pore volume of charcoal from coffee grounds were increased with increases in the carbonization temperature. The mean pore diameter diminished with increases in the carbonization temperature. However, these values were smaller than those of activated carbon. In general, properties of activated carbon are as follows: 700–1500 m²/g in specific surface area, 0.5–1.0 ml/g in pore volume and 12–30 Å in mean pore radius.[13]

Table 1. Properties of Charcoals from Coffee Grounds

charcoal	specific surface area (m²/g)	pore volume (ml/g)	mean pore radius (Å)
A	0.17	0.001	72.6
B	13.98	0.012	17.4
C	61.71	0.041	13.3

A: carbonized at 800°C, B: carbonized at 1000°C, C: carbonized at 1200°C.

Table 2. Equilibrium Amount of Acid Orange 7 Adsorbed onto Charcoals from Coffee Grounds at 25°C

charcoal	amount adsorbed (mg/g)		
	at 10 mg/l[a]	at 100 mg/l[a]	at 500 mg/l[a]
A	0.21	1.01	3.09
B	0.39	3.12	13.38
C	1.71	6.02	14.51

A: carbonized at 800°C, B: carbonized at 1000°C, C: carbonized at 1200°C. Charcoal dose, 0.05–0.2 g/30 ml; initial dye concentration, 50–1000 mg/l; Agitation time, 20 days; temperature, 25°C. a) equilibrium dye concentration.
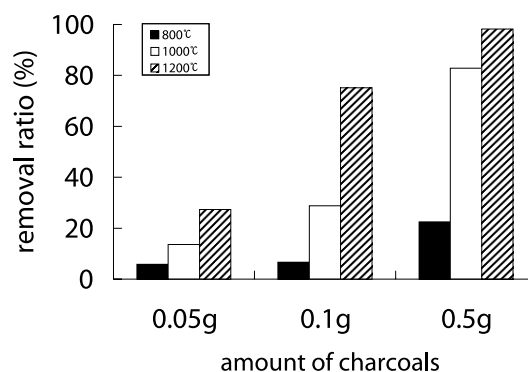

Fig. 1. Removal Ratio of Acid Orange 7 onto Charcoals from Coffee Grounds

Adsorbent dose, W (0.05–0.5) g/30 ml; initial dye concentration, 10 mg/l; temperature, 25°C.

The equilibrium amounts of acid orange 7 adsorbed onto charcoals in several equilibrium concentrations were calculated by the application of the Freundlich equation. The results are indicated in Table 2. The equilibrium amounts of acid orange 7 adsorbed onto charcoals were larger in charcoal carbonized at higher temperature.

The ratio of acid orange 7 removal by the addition of charcoal is shown in Fig. 1. The ratio of acid orange 7 removal increased with the weight of charcoal added. And the removal ratio by charcoal carbonized at a higher temperature was also increased. The removal ratio by charcoal carbonized at 800°C
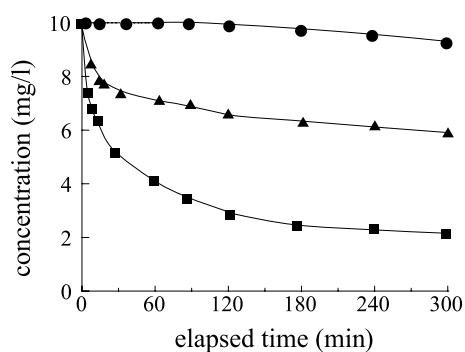
Fig. 2. Change in Acid Orange 7 Concentration with Elapsed Time

●: 800°C, ▲: 1000°C, ■: 1200°C. Adsorbent dose, 3.0 g/300 ml; initial dye concentration, 10 mg/l; stirring, 200 rpm; temperature, 25°C.
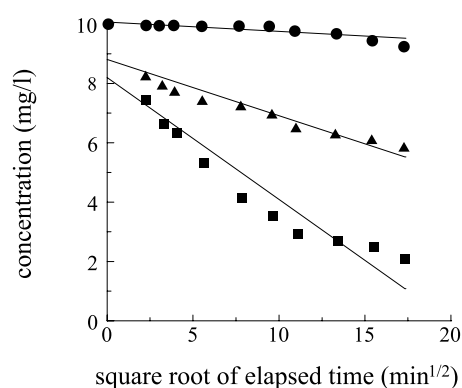

Fig. 3. Intraparticle Diffusion Plot for Adsorption of Acid Orange 7

●: 800°C, ▲: 1000°C, ■: 1200°C. Adsorbent dose, 3.0 g/300 ml; initial dye concentration, 10 mg/l; stirring, 200 rpm; temperature, 25°C.

Table 3. Kinetic Constants of Acid Orange 7 Adsorption by Charcoals from Coffee Grounds

charcoal	kinetic constants	
	$(mg/l \cdot min^{-1})^{a)}$	$(mg/l \cdot min^{-1/2})^{b)}$
A	0.002 (R = 0.963)	0.038 (R = 0.873)
B	0.009 (R = 0.811)	0.189 (R = 0.921)
C	0.020 (R = 0.819)	0.411 (R = 0.939)

A: carbonized at 800°C, B: carbonized at 1000°C, C: carbonized at 1200°C. R: correlation coefficient. a) the absolute values of the slope of regression line from Fig. 2. b) the absolute values of the slope of regression line from Fig. 3.

DISCUSSION

Our socioeconomic activities and current lifestyles are made possible by the use of immense resources and massive discharge of waste materials, some of which are not decomposed by natural processes. These waste products are discharged as refuse, exhaust gas and waste water into the environment. This problem is typically manifested in the discharge of waste in quantities far exceeding the disposal capacities and the serious lack of sites for final disposal. Qualitatively, also, there are problems due to the generation of dioxins during the burning of waste and contamination by heavy metals caused by efflux of water from the final dumping sites. Such quantitative and qualitative burden of waste on the environment not only exerts adverse effects on present economic activities and living environment but also will be a negative legacy burdening future generations.

To appropriately resolve these problems and to minimize the burden of waste on the environment, it is necessary to see that materials are circulated continuously in a manner desirable for environmental preservation and to take relevant and unceasing environmental safegurd measures throughout the entire course of the circulation of materials. From this background, "The Basic Law for Establishing a Recycling-based Society" was enacted in June 2000.

Consumption of coffee has increased, and the amount of discharged coffee grounds has also increased. A portion of the coffee grounds is reused, but most are disposed by burning.

In this investigation, we discussed the adsorption removal of acid orange 7 by charcoal from coffee grounds. The specific surface area and pore volume of charcoal were increased with the increase in carbonizing temperature. In general, the dominant factor of adsorption for organic pollutants is the spe-

was small, however, that by charcoal carbonized at 1200°C was almost adequate.

In evaluating an adsorbent, the kinetics for dye removal is another factor to be determined. The time courses of acid orange 7 removal by charcoals are shown in Fig. 2. The degree of reduction in acid orange 7 concentration over time using charcoal carbonized at 800°C was small, while that by charcoal carbonized at 1200°C was greater than that by charcoals carbonized at either 800 or 1000°C.

By the use of data shown in Fig. 2, the relationships between the concentrations of acid orange 7 and the square root of elapsed time are shown in Fig. 3. A good linear relationship was recognized. Then the slope of the line in Figs. 2 and 3 as a kinetic constant was calculated, and indicated in Table 3. Charcoal carbonized at a higher temperature indicated a larger value of kinetic constant.

cific surface area and pore volume.[14,15] The differences in the amount of acid orange 7 adsorbed and the removal ratio could be explained by differences in the physical properties of charcoal.

In the relationship between the residual concentration of acid orange 7 and the square root of elapsed time, a good linearity was recognized. Annadurai *et al.*[16] reported that the relationship between the amount of Rhodamine 6G adsorbed onto activated carbon and the square root of elapsed time demonstrated a linear characteristic, therefore, the adsorption process is controlled by the intraparticle diffusion. The adsorption rate of acid orange 7 onto charcoal from coffee grounds could be controlled by intraparticle diffusion.

It is suggested that charcoal from coffee grounds as a food waste is useful for acid orange 7 removal. Moreover, an activation process for charcoal is required to increase the adsorption ability.

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