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Characteristics of the Adsorption of Dissolved Organic Matter by Charcoals Carbonized at Different Temperatures

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Abstract

We investigated the adsorptive volume and rate, adsorption isotherm, and the pH dependence of charcoals obtained from carbonizing cedar (*Cryptomeria japonica* D. Don) wood chips at various temperatures; these charcoals were used to remove dissolved organic matter (DOM) that was eluted from rice-straw. In order to confirm the adsorption characteristics, three experiments were carried out in the laboratory. The adsorption characteristics were estimated by determining the total organic carbon (TOC) concentration, adsorption isotherm and the pH in solutions. Results showed that the trend of DOM adsorption effect by charcoals was categorized into two groups: group-1 (charcoals carbonized at less than 750ºC) and group-2 (charcoals carbonized at more than 850ºC). Group-2 adsorbed a greater amount of DOM and at a more rapid rate than group-1. The adsorption isotherm for group-2 followed the Freundlich model. In particular, the Freundlich constants, K and 1/N, for the charcoal carbonized at 1,050ºC indicated that this charcoal had higher adsorption volume and adsorption intensity for DOM than other charcoals. Furthermore, this charcoal adsorbed TOC irrespective of the initial pH value in sample water. This indicated that charcoals carbonized at 1,050ºC could change the pH value of the water contaminated with acid to neutral.

Discipline: Agricultural environment
Additional key words: cedar wood, Freundlich isotherm, pH dependence, rice-straw water

Introduction

Wood charcoals have many possible usages owing to their physical or chemical properties. They are often used as adsorbent materials, for example in deodorizers, soil conditioners and humidity controllers.

Wood charcoal is a porous material. Several important characteristics of porosity are the specific surface area, pore size, pore volume, and the spatial distribution of pores within the charcoal particle. The porous properties of charcoals depend on the carbonizing conditions such as the carbonization temperature, the drying time and the presence of air during carbonization. The porosity of charcoals changes depending on the carbonization temperatures and plays a significant role in adsorption. In particular, the formation of micropores and the size of specific surface areas were considered to be important factors for adsorption. Some researchers have reported that wood charcoals carbonized at 600ºC, 1,000ºC, 1,200ºC, and 1,400ºC could remove mercury, but those carbonized at temperatures above 1,600ºC could not[12,13]. In addition, the adsorption of iodine by charcoals carbonized at 700ºC, 800ºC and 900ºC was high, but that by charcoals carbonized at 1,000ºC was low[3].

Recent concerns regarding the aquatic environment have focused on the dissolved organic matter (DOM) that leads to the deterioration of the water environment in closed water bodies downstream. These concerns have arisen because DOM, particularly recalcitrant DOM, is a potential source of the carcinogen trihalomethane, which is produced during chlorination in water purification plants[4,7]. Moreover, there is a concern that the excessive use of fertilizers in agricultural fields affects the environ-

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ment since water percolates through acidified soil[6], and greenhouse culture causes alkalization or acidification of the soil by salt accumulation or the repeated application of fertilizers[10,11].

One of the sources of DOM includes agricultural fields, which are nonpoint sources of pollution. DOM consists of hydrophobic organic acids, which when discharged from agricultural fields, may include humic substances derived from plant matter[16].

In this study, we investigated the DOM adsorption properties of charcoals carbonized at different temperatures by conducting an adsorption experiment. In order to examine the relation between DOM and charcoal adsorption, the adsorption isotherm was analyzed using the Freundlich model. Moreover, we examined the influence of pH on DOM adsorption.

Materials and methods

1. Preparation of charcoals

The carbonized charcoals used in this study were prepared from thin wood chips of cedar wood (*Cryptomeria japonica* D. Don). The charcoal prepared from coniferous trees such as cedar are reported to have larger total pore volumes and adsorption rates than those prepared from broad-leaved trees[2,17]. Charcoals carbonized at temperatures ranging from 650ºC to 1,050ºC with intervals of 100ºC (hereafter, C650, C750, C850, C950, and C1050) were produced at the carbonization factory of the Forestry Cooperative of Fukushima Prefecture, Japan.

In order to determine the physical characteristics of the charcoal, the specific surface areas (the surface area of the charcoal particle per mass) and pore volumes were investigated by the Brunauer-Emmett-Teller (BET) method. The surface structures of each charcoal were observed using a scanning electron microscope. Figure 1 and Table 1 show the scanning electron micrographs and the physical characteristics of all charcoals used in this study. The sizes of the pores depend on the carbonization temperatures. The higher the carbonization temperature of the charcoal increased, the smaller the size of the pores on the charcoal surface became. On average, the micro-

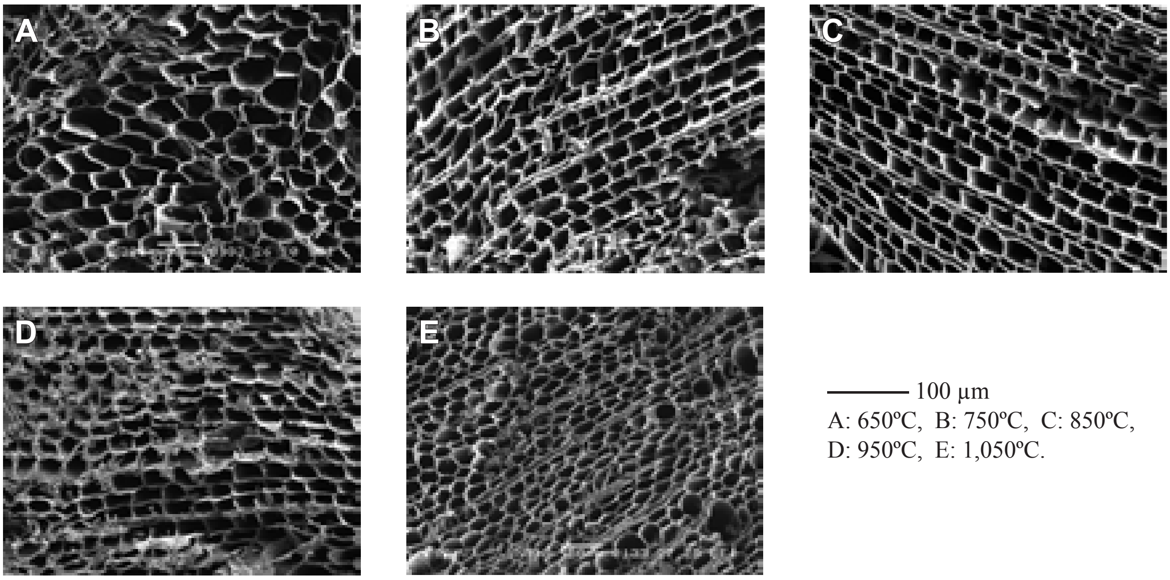

Fig. 1. Scanning electron micrographs of charcoals

Table 1. Physical characteristics of charcoals carbonized at 650ºC, 750ºC, 850ºC, 950ºC, and 1,050ºC

	Specific surface area (m^2/g)	Pore volume (mL/g)	Mean pore diameter (nm)	Mean particle diameter (mm)
C650	58.5	0.04	4.6	1.2
C750	78.0	0.09	5.6	1.4
C850	225.4	0.17	2.3	1.4
C950	203.5	0.15	3.9	1.5
C1050	224.0	0.12	2.7	1.6

The specific surface area refers to the surface area of the charcoal particle per unit mass.

pores of C1050 were 0.5 times larger than those of C650 as observed by the microscope (Fig. 1). The specific surface areas and pore volumes of C850, C950 and C1050 drastically increased (Table 1).

All charcoals used in the experiments were prepared to a size range of 1–5 mm and washed with distilled water.

2. Adsorption experiment with charcoals

The DOM adsorption experiment was performed by a contact oxidation method. A solution with DOM was prepared from aerated tap water in which rice straw had been immersed for approximately three months (hereafter rice-straw water). The charcoals (12 g) were placed in bottles with 800 mL of the rice-straw water. The sample waters in the bottles were continuously aerated at 20 ± 1ºC. Rice-straw water without charcoal was used as a control. We removed the sample water by amounts of about 20 mL from the bottles after 0, 0.25, 0.5, 1, 6, 10, 24, 48, 120, and 144 h of immersing the charcoals in the rice-straw water. We did not add water to the sample water in bottles. These methods had no major negative effect on the following results, because the required value in the experiment was not the time variation of total DOM volume but that of DOM concentration. The samples were filtered through membrane filters (pore size, 0.2 µm; J0511-155, Whatman, USA); the elution from the membrane filters was negligible. The DOM adsorption onto charcoals was estimated by determining the total organic carbon (TOC) concentration. The TOC in the samples was analyzed to be nonpurgeable organic carbon by means of the 680ºC combustion catalytic oxidation/nondispersive infrared method (TOC-V; Shimadzu Co., Japan).

3. Adsorption isotherms

In order to examine the relation between the TOC equilibrium concentration and the maximum adsorption volume of the charcoal, we conducted an experiment by varying the initial TOC concentrations of the rice-straw water between 3.5 and 20 $\mathrm{mg \cdot L^{-1}}$ through dilution. The charcoals (12 g) were placed in bottles with 800 mL of the rice-straw water, as was done in the adsorption experiment. The adsorption isotherms for the TOC concentrations were estimated from the results of the experiment using samples taken at 144 h, when they were considered to be stable.

The adsorption isotherms were analyzed by the Freundlich equation (Eq. 1).

$$\log(X) = \frac{1}{N} + K\log(C) \qquad \text{(Eq. 1)}$$

where C is the TOC concentration at 144 h ($\mathrm{mg \cdot L^{-1}}$); X is the adsorbed volume per volume of the adsorbent ($\mathrm{mg \cdot g^{-1}}$); and K and $1/N$ are the Freundlich adsorption constants, which depend on the adsorption temperature and the properties of the adsorbent and adsorbate. K is related to the adsorption volume and the adsorption intensity between the adsorbent and the adsorbate, and $1/N$ is related to the adsorption intensity of the adsorbent[14]. This equation shows the relationship between the adsorption volume and the equilibrium concentration under the conditions of a constant temperature and an adsorption interaction potential constant. It applies to the liquid phase adsorption at a narrow concentration range.

4. pH Dependence of adsorption capacity

We investigated the influence of pH on the DOM adsorption in the water samples treated with C1050, which demonstrated the most efficient DOM adsorption in the adsorption experiments.

The initial pH values of DOM solutions were set at 2.88, 3.60, 5.12, 6.56, 8.02, 9.50, and 10.78 with the addition of 1.0 M HCl or 1.0 M NaOH. The charcoals (C1050; 12 g) were placed in bottles with 800 mL of the DOM solution, as was done in the adsorption experiment. The water samples were collected at 24, 42 and 66 h of the contact time. The TOC concentration and pH were measured using a TOC analyzer and a pH meter (WM-50EG; TOA Electronics Co. Ltd., Japan), respectively.

Results and discussion

1. DOM adsorption experiments

Figure 2 shows the results of the DOM adsorption

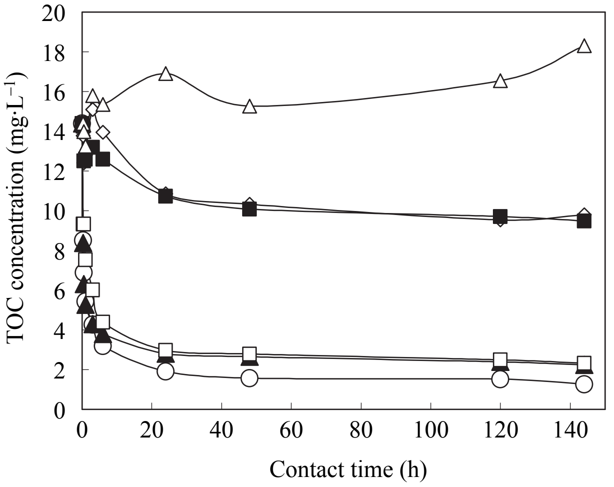

Fig. 2. Effects of the contact time on the TOC adsorption in the DOM solution containing charcoals

○ : C1050, ▲ : C950, □ : C850,
◇ : C750, ■ : C650, △ : Control.

experiments. The initial TOC concentration in the DOM solution was 14.4 mg·L^{-1}. To observe the decreasing trends of the TOC concentration, the charcoals were categorized as follows: group-1 (C650 and C750) and group-2 (C850, C950 and C1050). There was a large difference in the decreasing TOC concentrations between the two groups soon after beginning the experiment. For the first 10 h, the TOC concentration of group-2 decreased drastically, while that of group-1 decreased slowly.

The efficiency of TOC adsorption by charcoals is shown in Table 2. For the first 0.25 h, the adsorption rate of group-2 was 35.2–41.9%, while that of group-1 was 1.0–4.3%. After 24 h, the adsorption rate of group-2 was approximately 70% and that of group-1 was less than 30%; the adsorption rate of C1050 reached over 90% after 144 h. The TOC concentration in the control water increased with fluctuation throughout the test. This increase is attributed to the fact that the carbon in the air may dissolve in the sample water.

The specific surface area of group-2 was approximately thrice as large as that of group-1, and the pore volume of group-2 was approximately twice as large as that of group-1 (Table 1). These results suggest that the adsorption property is related to the physical characteristics of the adsorbent. In other words, group-2, which had a large specific surface area and pore volume, adsorbed a greater amount of the DOM and at a quicker rate than group-1.

Generally, the absorption onto activated carbon and wood charcoal depends on the London dispersion force of der Waals' forces[9]. When an adsorbate molecule sits at a point close to the wall of a pore, it is adsorbed by a large force. In other words, the smaller the pore the charcoal has the larger the dispersion force. The adsorptive characteristics depend on the relationship between the size of the adsorption molecule and the pore diameter of the adsorbent, irrespective of the kinds of molecule.

In a report about the adsorption of phenols from a solution which was dissolved phenol in purified water[5], they described that the phenol adsorptive volume by the charcoal with a small pore size was higher than that of charcoal with a large pore size. Their result was explained as follows; the process of liquid phase adsorption is explained by Polanyi's theory of adsorption potential[1]. That is, when molecules dissolved in solution were separated from a solvent and concentrated in the pore interior, the energy which causes this phenomenon to occur depended on the small pores which had large dispersion force.

On the charcoals used in this study, as shown in Table 1, the mean pore diameter of group-2 was smaller than those of group-1. Therefore, our results from the experiment supported the findings that the adsorption intensity was higher on the surface of a pore from group-2 than that of group-1.

Table 2. Comparison of the rate of TOC adsorption by charcoals at 0.25, 24 and 144 h

Contact time (h)	Adsorption rate (%)				
	Group-1		Group-2		
	C650	C750	C850	C950	C1050
0.25	1.0	4.3	35.2	41.9	40.9
24	25.5	24.6	79.3	80.5	86.6
144	30.6	31.5	79.7	84.4	91.2

2. Adsorption isotherms

The adsorption isotherms for all charcoals were analyzed using the Freundlich model, except for one outlier that had affected the results of our analysis. The Freundlich adsorption constants, K and $1/N$, were identified by the least-square method. The correlation coefficient and the Freundlich adsorption constants are shown in Table 3, and the correlation charts are shown in Fig. 3. Group-2 (C850, C950 and C1050) showed higher regression coefficients (R = 0.99–0.96). While, group-1 (C750 and C650) showed low regression coefficients (R = 0.38 and 0.40) (Table 3). The value calculated using the Freundlich model agreed well with that observed in group-2 (Fig. 3).

The constant K, which indicates adsorption volume, increased with rising carbonization temperatures. The constant $1/N$, which indicates adsorption intensity, was similar for C850 and C950 (Table 3). This suggested that the surface structures of both these charcoals, which show the chemical properties of the functional groups on the surface, were similar. C1050 had high adsorption intensity because the constant $1/N$ for C1050 was larger than that for the other two charcoals in group-2 (Table 3). Moreover, when the adsorption constants were compared

Table 3. Correlation coefficient between the values calculated by the Freundlich model and those measured using the Freundlich isotherm constants

Charcoal types	Correlation coefficient	Freundlich isotherm constants	
	R	K	$1/N$
C650	0.4	0.27	0.11
C750	0.39	0.27	0.18
C850	0.99	0.25	0.88
C950	0.99	0.38	0.82
C1050	0.96	0.46	1.95

Contact time = 144 h.

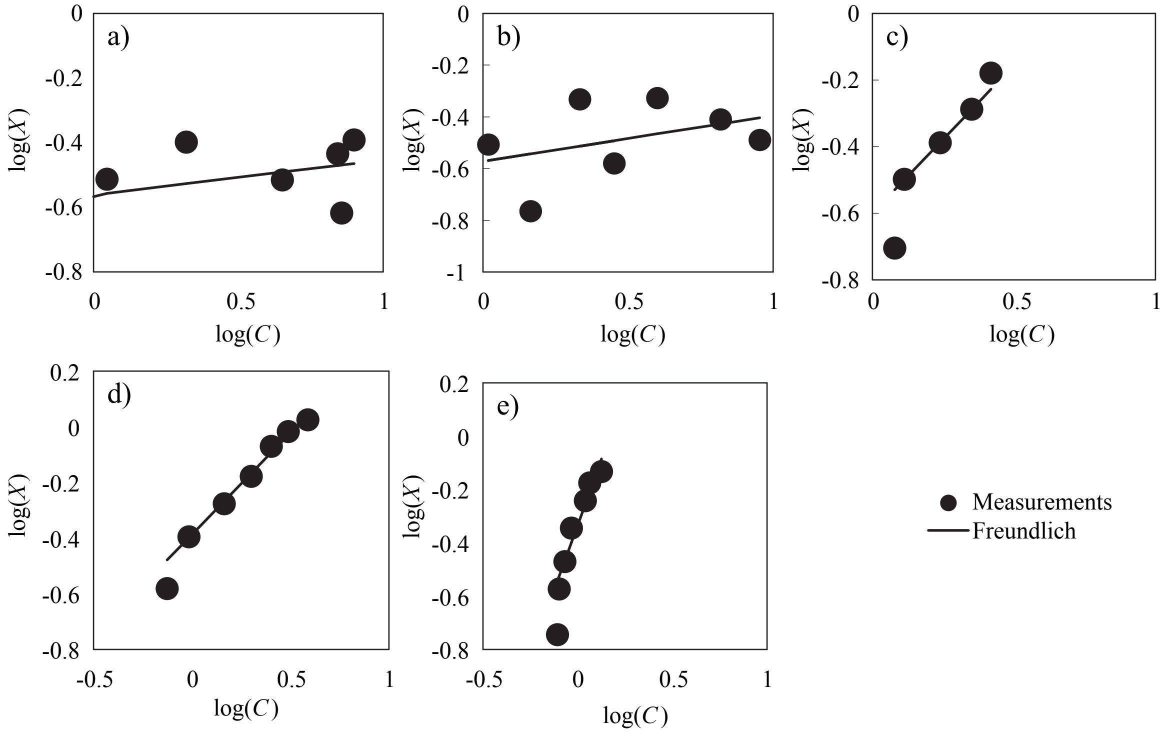

Fig. 3. Correlation between the Freundlich adsorption isotherms and the isotherms for TOC adsorption onto (a) C650, (b) C750, (c) C850, (d) C950, and (e) C1050

to the physical characteristics of the charcoal, both *K* and 1/*N* increased with a decrease in the pore volume (Table 3). This is because charcoal underwent thermal contraction, and the pore volume decreased with increasing carbonization temperatures; as a result, the adsorption volume and intensity increased with the development of many small pores.

In addition, the constants *K* and 1/*N* for group-1 were different from those for group-2 because there was no correlation between the adsorption isotherms calculated for group-1 and those obtained by using the Freundlich model (Table 3).

3. pH Dependence

The time changes in the adsorption rate of the water samples are shown in Table 4. The initial TOC concentrations were 26–29 mg·L^{-1}. The adsorption rate was highest in the water samples with an initial pH of 2.88. In the experiment on DOM adsorption by charcoals, this value tended to be higher in acidic solutions than in alkaline solutions (for example, 95% adsorption rate at pH 2.88; 80% adsorption rate at pH 10.78) (Table 4). The adsorption rates of all samples were over 70% at 66 h irrespective of the initial pH value. Additionally, the pH of all sample waters reached an approximate value of 8, except that for one solution in which the pH was 2.88 (Table 5).

The chief adsorption characteristics of carbon are the pore structure and the chemical functional groups on the surface. The latter characteristic of charcoals depends on the production conditions such as the carbonization temperature. The chemical properties of charcoal surfaces affect the adsorption characteristics of charcoals. It is known that the adsorption mechanism can be explained chemically and depends on the pH of the adsorbent[15].

Hitomi et al.[5] examined HCl and NaOH adsorption volume onto cedar charcoals carbonized at a variety of temperatures (400ºC to 900ºC with intervals of 100ºC) in order to investigate chemical characteristics of their surface. Their results showed that the HCl adsorption volume increased sequentially on charcoal carbonized at low to high temperature. While, NaOH adsorption volume was small at over 600ºC. According to the report of the relationships between carbonization temperature and functional groups on the inner surface of charcoal[8], the acidic groups related to basic adsorption drastically decreased from charcoal surfaces carbonized at between 450ºC and 550ºC.

We assumed that if wood was of the same kind and the carbonization temperatures were similar, the surface chemical structure would be also mutual. That is, it was considered that the cedar charcoal used in our study was similar to the properties for that used in the study of

Table 4. Time change in the adsorption rate in the sample waters

Contact time (h)	Initial pH value						
	2.88	3.6	5.12	6.56	8.02	9.5	10.78
	Adsorption rate (%)						
0	0	0	0	0	0	0	0
24	86.9	75.0	73.8	73.3	74.2	70.8	68.1
42	87.6	81.7	78.0	77.7	76.5	74.7	73.2
66	91.6	82.6	81.2	81.3	79.1	78.2	77.0

Table 5. Time change in the pH value in the sample waters

Contact time (h)	Initial pH value						
	2.88	3.6	5.12	6.56	8.02	9.5	10.78
	Time change in pH						
24	5.6	7.9	8.1	8.3	8.3	8.6	9.2
42	5.9	8.1	8.2	8.3	8.4	8.5	8.8
66	6.1	8.1	8.2	8.3	8.4	8.5	8.8

Hitomi et al.[5]. However, our experimental results were different from their results. The reason for this could be considered as the following; in their experiment, the adsorption interaction between charcoal and inorganic ions could be explained as the phenomenon of the cation exchange action on the surface of charcoal. While, in our experiment, the adsorption interaction between charcoal and DOM might be explained as the effect of the chemical structure of DOM. DOM has amorphous and various complicated chemical structures[16,18]. The functional groups of DOM with humic substances consist of carboxyl groups, carbonyl groups, amino groups, and so on, which show the variety of an acidic dissociation constant[18]. Therefore, the DOM adsorption onto charcoal would depend on the chemical structure characteristics of DOM.

Additionally, it was also considered that since charcoal came into contact with DOM through the circulating aerated waters, the collision between the two surfaces facilitated DOM adsorption.

Consequently, C1050 adsorbed TOC irrespective of the initial pH value in the sample water. Moreover, it indicated that C1050 could change the pH value of acid water to neutral.

Conclusions

In this study, we conducted the experiments by using rice-straw water to determine the DOM adsorption volume and rate, and the pH dependence of cedar wood charcoals produced at several carbonization temperatures. The trend of the DOM adsorption effect by charcoals was categorized into two groups: group-1 (C650 and C750) and group-2 (C850, C950 and C1050). Group-2 adsorbed a greater amount of DOM than group-1. In addition, the adsorption isotherms obtained for group-2 agreed well with the value calculated by the Freundlich model. In particular, the Freundlich adsorption constants, K and $1/N$, for C1050 indicated that C1050 had the higher adsorption volume and adsorption intensity for DOM than other charcoals. Furthermore, the adsorption rates of all samples treated by C1050 were over 70% for adsorption ratio irrespective of the initial pH value. Observation of the pH dependence showed that the adsorption in acidic solutions tended to be higher than that in alkaline solutions. Moreover, it indicated that C1050 could change the pH value of water contaminated with acid to neutral.

Our results showed that the charcoal carbonized at higher temperature (group-2) much more efficiently removed the DOM from the rice-straw water. It can be expected that the charcoal will be used as an adsorbent, for example as a filling material for under-drains and filtering material in farm drains, and for removing organic matter from agricultural drainage water including DOM. Although our results demonstrated that the charcoal removed organic matter from the rice-straw water in a lab test, removal efficiency (rate or volume) can be dependent on the contact time between charcoal and drainage water, and the concentration of drainage water in situ. To purify the drainage water by equipment using the charcoal, further research on the mechanisms of nutrient and TOC removal are needed.

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