Preparation and adsorption performance evaluation of activated carbon fibers derived from rayon

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Abstract

Activated carbon fiber (ACF) is a material that has attracted significant attention because ACFs derived from several fiber sources have been adapted as filter materials. Here, we described successful ACF preparation via single- and two-step thermal treatments of rayon. Methylene blue adsorption abilities of the resulting ACFs were evaluated. Results indicated that ACFs derived from rayon which is prepared by the two-step thermal treatment demonstrate adsorption ability. Moreover, the average gray-scale intensities (GIs) of the carbonized samples were obtained from images captured with a common digital camera, and the results exhibited meaningful correlations for both yield and absorption ability with GI. Correlation between GI and absorption ability suggests the potential for a simple, nondestructive method of evaluating the absorption ability of ACFs. Results obtained for rayon is easily transferred to other fiber products or industrial waste materials generated during the manufacture of textiles that offers potential energy savings.

Keywords Activated carbon fiber · Rayon · Adsorption · Thermal treatment

1 Introduction

Carbon related materials such as carbon nanotubes are focused as their electronic properties [1, 2]. Recently, activated carbon fibers (ACFs) are known as carbon related materials. ACFs derived from several fiber sources have been adapted as filter materials [3, 4]. ACFs exhibit strong adsorption performance, which is generally higher than that of conventional activated carbon [3–5]. Several methods for the preparation of ACFs, such as chemical modification and heat treatment have been studied; however, the adsorption abilities of ACFs could be potentially improved by ACF preparation methods. Rayon is a well-known synthetic fiber widely used in the production of textiles that has served as a focus of ACFs [6].

Recently, the activation of several different types of carbon sources has also been evaluated [7–9]. Our group has

focused on waste materials from clothes. Clothes are made from many kinds of fibers such as cotton, silk polyesters, rayon, and so on. We reported producing activated carbon fibers from silk, cotton and polyester and fiber mixtures from cotton, polyester, and rayon [10–13]. Because rayon is a textile fiber, it is expected to be obtainable as a recycled material. It has been reported that the amount of refuse fiber materials in Japan is approximately 1,712,000 t per year [14]. The productions of ACFs derived from recycled rayon fibers can serve to decrease the burden associated with this refuse and result in substantial energy savings.

Common evaluation procedures for ACF adsorption performance involve methods such as methylene blue (MB) adsorption [15–17], nitrogen adsorption [8, 18] and iodine [19] conventionally. Generally, the process of making ACFs need some steps and spent time, such investigation processes for ACF adsorption performance

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should consume some samples of ACFs. It is expected to investigate the performance without sample consumption. Therefore, we have tried to develop the evaluation of absorption ability for ACF in non-destroy evaluation systems referring to other research [20] using XRF [10]. We also have tried another non-destroying methods for ACFs using common digital camera [10–12] referring to other group which tried to evaluate produced era for important old traditional materials [21, 22].

In this study, we prepared ACFs from rayon using two thermal treatment processes with varying parameters, and the MB adsorption of the resulting samples was evaluated.

Such methods have a shorter point because the sample consumptions were needed.

ACFs with good adsorption performance from rayon fiber could be successfully obtained. Moreover, the average gray-scale intensities (GIs) of the carbonized samples were obtained from images captured with a common digital camera, and the results exhibited meaningful correlations for both yield and absorption ability with GI. The correlation between GI and absorption ability suggests the potential for a simple, nondestructive method of evaluating the absorption ability of ACFs.

2 Materials and methods

2.1 Materials

Rayon was purchased from the Japanese Standards Association. Cotton was obtained from Nittobo Niigata Co, Ltd. MB, potassium dihydrogen phosphate, and disodium hydrogen phosphate were purchased from Kanto Chemical (Japan). Activated charcoal made from waste palm shell (ACP) was purchased from Taihei Chemical (Japan).

2.2 Thermal treatment

The cotton samples were carbonized in a tubular furnace (ISUZU, KRO-14) at various temperatures using a temperature control unit (CHINO, MODEL-SU) under the flow of nitrogen or carbon dioxide gas. It needs around 2 h in increasing temperature and it was kept an hour on the maximum temperature. Thermal treatments for the activation all conducted at 900 °C in carbon dioxide gas (Tables 1 and 2). In advance, the samples were prepared from rayon or carbonized carbon by heat treatment from 400 to 600 °C in nitrogen.

2.3 Observation

The structural characteristics of each sample were examined using a scanning electron microscope (SEM; JEOL,

Table 1 Summary of the primary heat treatment processes employed

Materials	Heat treatment (°C)	Product (sample name)
Rayon (R)	Nitrogen gas R.T-900	R-900C
	Carbon dioxide gas 900	
	Nitrogen gas R.T-400	R-400N
	Nitrogen gas R.T-500	R-500N
	Nitrogen gas R.T-600	R-600N

JSM-6060A) [13, 23–25]. The images were processed using Image J software.

2.4 Adsorption of MB

Test methods for activated carbon given were referred in Japan Industrial Standard K-1474. Briefly, we began with a 1200 mg/L aqueous MB solution. Diluted the MB solution with a phosphate buffer was made from potassium dihydrogen phosphate, disodium hydrogen phosphate, and Milli-Q pure water to concentrations of 120, 24, 12, 2.4, 1.2, 0.24, and 0.12 mg/L. The optical absorbance of these solutions was measured using a spectrophotometer (U-3210, HITACHI, Japan) to obtain a calibration curve. The absorbance of the 120 mg/L MB solution was measured after adding 1 g of ACF, or ACP as a positive control, and shaking for 30 min by using vibration instrument (TAITEC, Saitama, Japan). Then absorption ability as the amount of MB (mg) adsorbed was calculated by the activated carbon absorbent (ACF or ACP [g]) based on the optical absorbance of the solution using the obtained calibration curve.

2.5 Simple evaluation of adsorption performance of ACFs

The adsorption performances of ACFs were also evaluated without the use of the spectrophotometer using images captured by a digital camera (Ricoh, caplioR5, lens focal length 4.6–33 mm) and subsequent processing using Image J software. The samples were photographed at a camera lens-to-sample distance of 30 cm. The method was based on previous methods used in the evaluation of liquid crystals [26–28] and ACFs derived from silk [10], cotton [13], polyester [11], and fiber mixture [12]. The color images were converted to gray-scale with pixel values from 1 to 255 using Image J software, and the average GI was used to quantify changes in the optical absorbance [10–12]. The average intensity was calculated based on more than 100 points from the gray-scale image.

2.6 Statistical tools

The correlation coefficient and standard deviation were calculated using the CORREL and STDEVP functions, respectively, incorporated into Microsoft Excel 2011.

3 Results and discussion

3.1 Sample labeling

Typical photos of the untreated and treated rayon (R) samples are shown in Figs. 1 and 2, respectively, and a summary of the heat treating processes employed are listed in Table 1. Figure 1 presents sample images of untreated rayon (a; R) and rayon heat-treated under carbon dioxide at 900 °C (b; R-900C). Figure 2 presents rayon samples heat-treated in nitrogen at 400 °C (a; R-400N), 500 °C (b; R-500N), and 600 °C (c; R-600N). In addition, as listed in Table 2, sample R-400N was subjected to secondary heat treatment in carbon dioxide at 900 °C (R-400N-900C), sample R-500N heat-treated in carbon dioxide at 900 °C (R-500N-900C), and sample R-600N heat-treated in carbon dioxide at 900 °C (R-600N-900C). For comparison, a cotton sample (NC) was heat-treated in nitrogen at 400 °C (NC-400N), as shown in Fig. 4.

Fig. 1 Images of rayon (**a**; R) and activated carbon fibers derived from rayon (**b**; R-900C; Table 1)

Fig. 2 Images of carbonized fibers derived from rayon by heat treatment under nitrogen at several temperatures (R-400N (**a**), R-500N (**b**), and R-600N (**c**); Table 1)

Table 2 Summary of the heat treatment processes employed in the second processing step

Materials	Heat treatment (°C)	Product (sample name)
R-400N	Nitrogen gas R.T-900 Carbon dioxide gas 900	R-400N-900C
R-500N	Nitrogen gas R.T-900 Carbon dioxide gas 900	R-500N-900C
R-600N	Nitrogen gas R.T-900 Carbon dioxide gas 900	R-600N-900C

3.2 Thermal treatment for carbonization

We first present the results of the ACF derived from rayon. ACF was successfully obtained in a single step by heat treatment at 900 °C in carbon dioxide (Fig. 1).

Next, ACFs were prepared from the rayon samples by a two-step thermal treatment because two-step heat-treatment of cotton has been shown to yield high adsorption performance. Cotton is known to carbonize by thermal treatment in nitrogen at 400 °C, and because both cotton and rayon mainly consist of cellulose, an equivalent treatment was expected to carbonize rayon as well. However, as shown in Fig. 2a, numerous white regions are observed on the rayon sample, indicating incomplete carbonization. Therefore, the heat treatment temperature was raised to 500 °C and 600 °C. As indicated by Fig. 2b, c, respectively, the sample was not fully carbonized at 500 °C, but that heat treatment at 600 °C resulted in a completely black sample. The average GIs of the rayon samples was also investigated, as shown in Fig. 3, where a low value is indicative of strong black, and consequently, a high degree of carbonization [10–12]. This suggests that the valuable evidence of carbonization can be obtained simply by visual inspection.

The condition of carbonization of rayon with that of cotton was compared. Previously, we reported ACF preparation from cotton purchased from the Japanese Standards Association. This study employed the cotton sample shown in Fig. 4a made from a different weave obtained elsewhere. However, the cotton sample employed in this study was found to be completely carbonized at 400 °C, as

Fig. 3 Average gray-scale intensities of untreated rayon (R) and rayon treated at several temperatures (R-400N, R-500N, R-600N, and R-900C; Table 1) based on more than 100 points from the image of each sample; the error bars represent the standard deviation of the measurements

Fig. 4 Images of the cotton sample (a; NC) and the carbonized fibers derived from (NC-400N)

Fig. 5 Average gray-scale intensities of untreated rayon (R) and cotton (NC) samples, and those treated at several temperatures (R-400N, R-600N, and NC-400N; Table 1) based on more than 100 points from the image of each sample; the error bars represent the standard deviation of the measurements

shown in Fig. 4b. The extracted average GIs of the rayon and cotton samples are compared in Fig. 5. While a very low GI was obtained for the cotton sample at 400 °C, an equivalently low GI for rayon required heat treatment at 600 °C.

Fig. 6 Typical SEM images of rayon (a) and cotton (b), and their average fiber diameters obtained from the images (c); the error bars represent the standard deviation of the measurements

The untreated rayon and cotton samples were examined using SEM, as shown in Fig. 6a, b, respectively, and the SEM images were employed to determine the respective fiber diameters. For each sample, the diameters of more than 30 fibers were measured, and the calculated averages and standard deviations of the fiber diameters are shown in Fig. 6. It was found that the fibers of both samples mainly consist of cellulose, and the average diameter of the cotton fibers was significantly smaller than that of the rayon fibers. It was tried to compare the degree of carbonization using GI, because GI values may be the index of carbonization of fibers. GI value of the cotton sample at 400 °C was almost equivalently to GI for rayon derived by heat treatment at 600 °C (Fig. 5). These results may be based on the property of surface area on each fiber. A larger diameter indicates that each fiber has a larger surface area, and the larger surface area of the rayon fibers is the likely cause of the higher temperature required to carbonize the rayon samples relative to that of the cotton sample.

3.3 Thermal treatment for activation

Thermal treatments for the activation of carbonized rayon were all conducted at 900 °C in carbon dioxide gas (Table 2). In advance, carbonized samples were prepared from rayon by heat treatment from 400 to 600 °C in

Fig. 7 Images of activated carbonized fibers subjected to secondary treatment at 900 °C in carbon dioxide (R-400N-900C (a), R-500N-900C (b), and R-600N-900C (c); Table 2)

Fig. 8 Average gray-scale intensities of untreated rayon (R), rayon subjected to secondary treatment at 900 °C in carbon dioxide (R-400N-900C, R-500N-900C, and R-600N-900C; Table 2), and rayon subjected to primary treatment alone (R-900C; Table 1) based on more than 100 points from the image of each sample; the error bars represent the standard deviation of the measurements

nitrogen. These samples were used to prepare the ACFs. As shown in Fig. 7, all samples were fully black, where their GIs are shown in Fig. 8.

3.4 Sample yields

The samples yields, which were calculated with the method used by Martinez et al. [29], were 16.05%, 17.14%, 11.27%, and 16.80% for samples R-900C, R-400N-900C, R-500N-900C, and R-600N-900C, respectively, as shown in Fig. 9. Yields of activated carbon from cotton, walnut shells, and peach stones [29] have been reported to be 37.92%, 20.80%, and 22.2%, respectively. The yields obtained in this study were therefore not improved compared with the previously obtained result for cotton. For the processing of both R to R-900C and R to R-600N, the sample volumes decreased (Fig. 9), and the sample colors changed to strong black (Figs. 2, 3). Similarly, for the processing of both R-400N to R-400N-900C and R-500N to R-500N-900C, the sample volumes decreased (Fig. 9) and the sample colors changed to strong black (Fig. 6). Conversely, for the processing of R to R-400N and R to R-500N, neither the color (Fig. 2) nor volume (Fig. 9) changed to the same

Fig. 9 Activated carbon fibers with corresponding yields (R-900C, R-400N, R-400N-900C, R-500N, R-500N-900C, R-600N, and R-600N-900C; Tables 1 and 2)

extent as the other cases. These facts indicate that the change of the color to that of strong black and a dramatically decreasing volume were correlated. The correlation coefficient between the GIs and the yields was calculated ($r=0.88$) verifying the high degree of correlation between the two phenomena.

3.5 Adsorption

MB was chosen in this study because it is known to strongly adsorb on activated carbon materials [10–13, 15–17, 25]. The typical adsorption isotherms of MB obtained for ACP, R, R-900C, R400N-900C, R500N-900C, and R600N-900C are shown in Fig. 10. As shown in the figure, the adsorption obtained for samples R-400N-900C and R-600N-900C is nearly equivalent to that of ACP. MB adsorption values of ACFs derived from rayon by the two-step treatment were all greater than those obtained for the one-step preparation (R-900C). As was previously found for cotton, this study finds that the two-step thermal treatment is an effective method for the preparation of ACFs

Fig. 10 Methylene blue (MB) adsorption for activated charcoal made from waste palm shell (ACP) rayon (R), and activated carbon fibers (R-900C, R-400N-900C, R-500N-900C, and R-600N-900C; Tables 1 and 2) with an initial MB concentration of 120 mg/L and an initial sample weight of 1 g

derived from rayon. These results also indicate that the optimum temperature in the first step for good carbonization is approximately 500 °C because the MB adsorption of R-500N-900C was the highest of all prepared ACFs.

According to the above results, the ACF products derived from rayon by the two-step thermal treatment process demonstrate superior adsorption ability. The observed high adsorption performance indicates that the pore structure of these samples is well developed with a large surface area. The facts suggest that the two-step thermal treatment might be an efficient method to prepare ACFs for application to electric capacitors because activated carbon with smaller pores exhibits a higher performance as an electric capacitor. Because rayon is a popular textile material, rayon should be easily obtained from textile waste. Therefore, in the future, rayon may be useful as recycled material for the fabrication of electric capacitors.

3.6 Simple evaluation of ACF absorption ability

A simple, nondestructive evaluation method of ACF absorption ability would be of great benefit. However, MB adsorption methods used some sample of ACF [10–13, 15–17, 25]. Therefore, it was attempted to evaluate the ACF absorption ability from the GI value based on images obtained using a common digital camera. To evaluate the ACF absorption ability, the correlation between adsorption and the GI was calculated. Although the correlation coefficient obtained ($r=0.61$) was not large, the value indicates that MB adsorption and GI were somewhat correlated. The GI is related to light absorbance. It is possible that considerations of wavelength or brightness of the incident light may result in a better correlation. As such, with further development, the method may be useful for the simple evaluation of adsorption ability without sample destruction. Our findings suggest that the evaluation

of the adsorption ability of ACFs is possible from simple image analysis.

Conventionally, evaluation procedures for ACF adsorption performance investigated via some methods such as methylene blue (MB) adsorption [15–17], nitrogen adsorption [8, 18] and iodine [19]. These methods can directly measure the adsorption ability of ACFs though with sample consumption. ACFs preparation methods need a lot of trying and error even under the obvious strategy. During performance evaluation of ACFs, it will be a shorter point such methods need times and sample consumptions. Therefore, it is the best methods for performance evaluation of ACFs without sample consumptions with a short time. Our proposed methods of camera imaging for ACFs need less than half an hour without sample consumption which is suitable for the above factor even though it needs more improvement for just correlation with actual adsorption value. Therefore, the camera imaging method is a good candidate for characteristic methods for ACFs as non-destructive evaluation in the future.

4 Conclusion

It could be that successfully prepared ACFs from rayon fibers using two different heat treatment processes of varying parameters that characterized the products. The results of MB adsorption experiments revealed that the two-step thermal treatment is a suitable method for ACF preparation. These results may be readily transferred to other fiber waste generated during textile manufacture, and recycled textile fibers may enable significant energy savings. Furthermore, it could be found that the MB adsorption values and the average GIs of the samples were correlated, and we anticipate the possibility of a simple evaluation of the adsorption ability of ACFs without sample destruction.

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Compliance with ethical standards

Conflict of interest The authors have no conflict of interest as far as the present study is concerned, to the best of their knowledge.

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