Effects of two-step heat treatment on the structure of cotton-derived activated carbon fibres

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Abstract: Activated carbon fibre (ACF), a novel material, has attracted considerable research attention. The pore structures found on the surfaces of ACFs are strongly related to their functionality. Herein, ACF was prepared via a two-step thermal treatment of cotton. The diameters and width distributions of thus-prepared ACFs were characterised using scanning electron microscopy (SEM). SEM analysis also revealed that the pore structures on the surfaces of the cotton-derived ACFs were activated by carbon dioxide. Successful adsorption functionality of these ACFs was characterised using a methylene blue (MB) solution. The effects of the two-step thermal treatment and potential

applications of this methodology are also discussed. The proposed method can be used on other fibre products or industrial waste materials generated during the manufacture of cloth and fibres, and the generated ACFs can be used for energy-storage applications.

Keywords: activated carbon fibre; ACF; scanning electron microscope; thermal treatment; activation; pore structure.

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1 Introduction

Activated carbon fibre (ACF), a novel material, is attracting considerable research attention (Pandolfo and Hollenkamp, 2006; Sugumaran et al., 2012; Myoubudani et al., 2014, 2015) particularly because the pores on the ACF surfaces can potentially trap undesired substances. Consequently, ACF is expected to become a viable alternative to activated carbon, which has conventionally been used as a filter to eliminate waste products. Therefore, effective methods for preparing ACF have been investigated (Sugumaran et al., 2012; Myoubudani et al., 2014, 2015) and the chemical modification of the pores on the ACF surface has been further explored (Pandolfo and Hollenkamp, 2006). Recently, several carbon sources have been evaluated as candidates for activation. Consequently, preparing ACF from agricultural waste, such as banana peels (Pandolfo and Hollenkamp, 2006) and almond shells (Pragya et al., 2013), has gained considerable attention.

Activated carbon and ACF can be obtained by modifying surface structures and treatment conditions (Tehrani et al., 2014; Jo et al., 2014; Khalil et al., 2013). Generally, carbon dioxide or water vapour is used as the activating reagent for carbon activation (Shao et al., 2015). The addition of KOH after carbon dioxide (Khalil et al., 2013) has also been investigated. Carbon fibres, such as cellulose, undergo thermal degradation at

160°C–400°C, carbonisation and pyrolysis at 260°C–800°C and graphitisation at 1,600°C. Therefore, the optimum temperature for carbonisation and activation appears to be ~900°C (Ioannidou and Zabaniotou, 2007). Although the pore size distribution is largely dependent on chemical properties of the carbon source (Mangun et al., 1998; Hu et al., 2001), the effects of different treatment methods on the pore size distribution have not been yet reported.

Heat treatment of cotton has been investigated as an ACF preparation method (Salehi et al., 2017; Yoda et al., 2018a, 2018b). Salehi et al. (2017) reported ACF derived from cotton was heated at 500°C using phosphoric acid as the activating reagent to enhance adsorption capacity and process yield. We have previously produced ACF from various fabrics, such as cotton, via a heating process (Yoda et al., 2018a, 2018b). ACFs derived from cotton were produced via one-step heating at 200°C, 400°C and 600°C under nitrogen or carbon dioxide gas (Yoda et al., 2018a). However, for a two-step thermal treatment, sufficient limit of detection for activated carbon has not yet been reported (Ooi et al., 2013).

Herein, ACF is prepared via two-step thermal treatment (Ooi et al., 2013) of cotton and the effect of thermal treatment on pore size distribution is discussed. Thermal treatment was performed in a tubular furnace because of its simple design; this furnace has been previously used for producing activated carbon (Yoda et al., 2017; 2018a, 2018b). Scanning electron microscopy (SEM) was used for micro-structural analysis (Barros et al., 2011; Fiorelli et al., 2012; Kaale and Katima, 2013; Mouri, 2014; Yoda and Mouri, 2015) and characterisation of the prepared ACFs (Japanese Industrial Standards, 2014; Myoubudani et al., 2014; 2015). A methylene blue (MB) solution was used to determine the adsorption functionality of the ACFs (Kaewprasit et al., 1998; Japanese Industrial Standards, 2014; Myoubudani et al., 2015; Yoda et al., 2017; 2018a, 2018b). Results revealed that the two-step thermal treatment is suitable for preparing ACF having adsorption functionality. The structures and functionality of ACFs prepared using several thermal treatment methods, such as one-step and two-step treatment using nitrogen and/or carbon dioxide gas, were also investigated.

2 Materials and methods

2.1 Materials

Cotton (single fibre cloth no. 670101) was purchased from the Japanese Standards Association. Cotton samples that were already heat-treated were provided by Nakatsuyama Heat Treatment Co., Ltd. MB, potassium dihydrogen phosphate and disodium hydrogen phosphate were purchased from Kanto Chemical (Japan). Activated charcoal made from palm (ACP) was purchased from Taihei Chemical (Japan).

2.2 Thermal treatment

The cotton samples were carbonised in a tubular furnace (ISUZU, KRO-14) having a temperature control unit (CHINO, MODEL-SU) under a flow of nitrogen or carbon dioxide gas at various temperatures.

2.3 SEM observation

Structural characteristics of each sample were examined using a scanning electron microscope (JEOL, JSM-6060A). Images were processed using Image J software.

2.4 Adsorption of methylene blue

We used the test method of Japan Industrial Standard K 1474 for measuring the adsorption of activated carbon (Yoda et al., 2017). We prepared a MB solution (1,200 mg/L), which was diluted with a phosphate buffer solution made from potassium dihydrogen phosphate, disodium hydrogen phosphate and milliQ pure water to prepare 120, 24, 12, 2.4, 1.2, 0.24 and 0.12 mg/L of solutions. The phosphate buffer solution was prepared by mixing 1/15 mol/l of potassium dihydrogen phosphate solution with 1/15 mol/l of disodium hydrogen phosphate solution in the ratio of 4:6. We measured the absorbance of these solutions and the phosphate buffer using a spectrophotometer (U-3210, Hitachi, Japan) to generate the calibration curve. Then, we separately added ACF and ACP (as a positive control) to two MB solutions (120 and 24 mg/L). The absorbance of the ACF and ACP solutions were simultaneously measured after shaking them for 30 min. The absorption was calculated from the calibration curve in units of mg MB per g ACF.

3 Results and discussion

3.1 Labels for the samples

The samples were labelled as follows: untreated cotton (C), cotton heat-treated in advance under nitrogen at 400°C (C-400N), cotton (C) heat-treated under nitrogen at 900°C (C-900N), cotton (C) heat-treated under carbon dioxide at 900°C (C-900C) and C-400N heat-treated under carbon dioxide at 900°C (C-400N-900C) (Table 1).

Table 1 Summary of heat-treatment processes

Materials	*Heat treatment*	*Product (sample name)*
Cotton (C)	Nitrogen gas at 900°C	C-900N
Cotton (C)	Carbon dioxide gas at 900°C	C-900C
Cotton (C) with nitrogen gas 400°C in advance (C-400N)	Carbon dioxide gas at 900°C	C-400N-900C

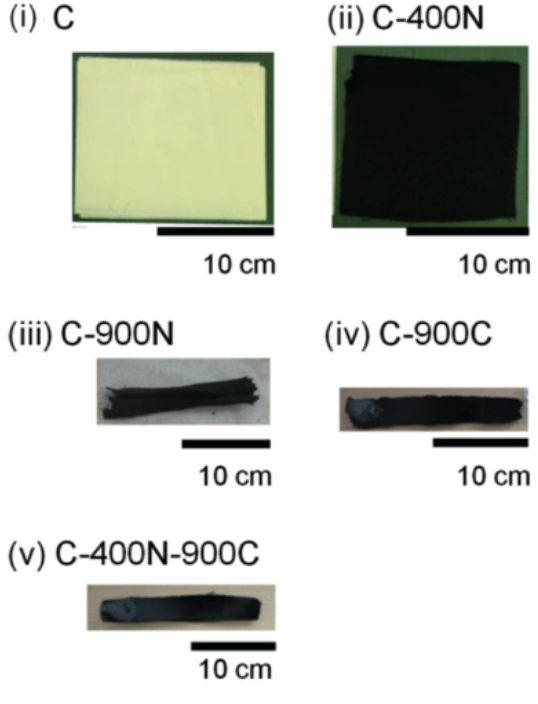
Note: Each process and sample name are listed.

3.2 Sample yields

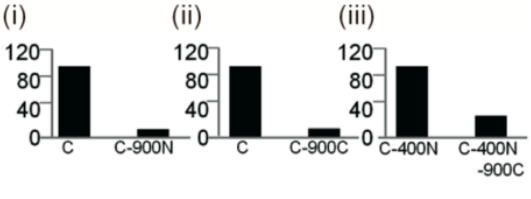
Typical photos of the untreated and treated cotton samples are shown in Figure 1(a). The heat-treated samples were fragile; therefore, images were obtained within the tube [Figures 1(a)(iii)–1(a)(v)]. The samples' yields calculated using the method proposed by Martinez et al. (2003) were 12.0%, 13.1% and 31.0% for C-900N, C-900C and C-400N-900C, respectively [Figure 1(b)]. Yields for activated carbon from cotton (Uddin et al., 2008), walnut shells and peach stones (Gopalakrishnan et al., 2019) were 37.92%,

20.8% and 22.2%, respectively. Most yields obtained herein were lower than those obtained previously for cotton (22%–25%) (Jain et al., 2013), whereas the yield of C-400N-900C was similar to that obtained previously [Figures 1(a)(iii)–1(a)(v)].

Figure 1 Images of cotton and ACFs with corresponding yields, (a) typical images: (i) cotton (C) (ii) C-400N (iii) C-900N (iv) C-900C and (v) C-400N-900C (b) yields: (i) C-900N, (ii) C-900C and (iii) C-400N-900C (see online version for colours)



(a)



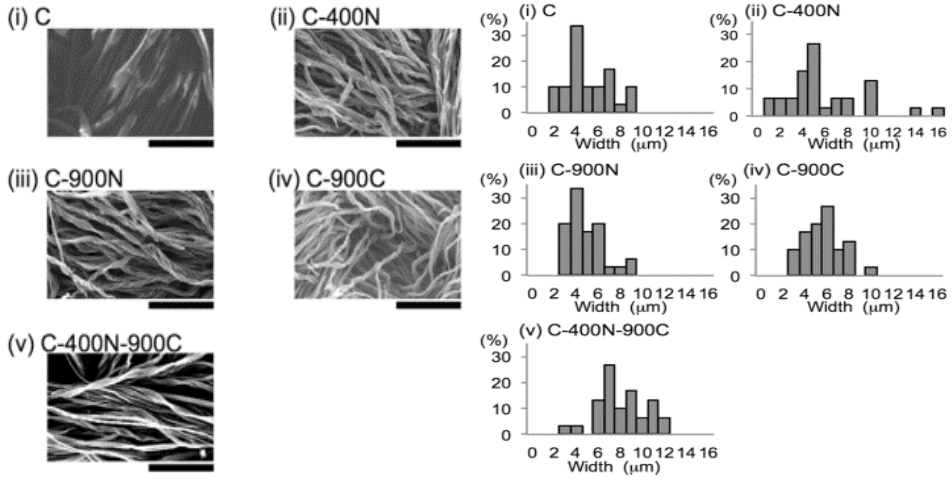
(b)

3.3 Diameters of the ACFs

SEM images of the fibres in each sample were obtained [Figure 2(a)] to determine their diameters. For each sample, diameters of at least 30 fibres were measured; distributions of the diameters are shown in Figure 2(b). For normal cotton, the fibre diameters were 2–10 μm [Figure 2(b)(i)]. Similarly, for C-400N, most fibre diameters were 2–10 μm although a few diameters were larger (14 and 16 μm) [Figure 2(b)(ii)]. For C-900N, the fibre diameters ranged from 3 to 10 μm [Figure 2(b)(iii)], whereas in the C-900C sample, most fibre diameters ranged from 3 to 8 μm, with very few larger fibres [Figure 2(b)(iv)].

Notably, for C-400N-900C, the fibre diameters were larger and ranged from 6 to 12 μm, with only a few smaller fibres [Figure 2(b)(v)]. Uddin et al. (2008) reported the diameters of coated cotton fibres to be ~15–20 μm; however, the cotton fibres used herein were much thinner. The diameters of the activated fibres in the sample pre-heat-treated under nitrogen and then heat-treated under carbon dioxide were relatively thicker than those in the untreated cotton or those treated only under nitrogen or carbon dioxide. Thicker fibres are expected to be advantageous because they would provide a larger surface area and trap more waste particles/substances.

Figure 2 SEM images of ACFs prepared under different activation conditions and their width distributions, (a) typical SEM images: (i) cotton (C) (ii) C-400N (iii) C-900N (iv) C-900C and (v) C-400N-900C, (b) scale bars indicate 100 μm, distributions of fibre widths: (i) cotton (C), (ii) C-400N, (iii) C-900N, (iv) C-900C and (v) C-400N-900C

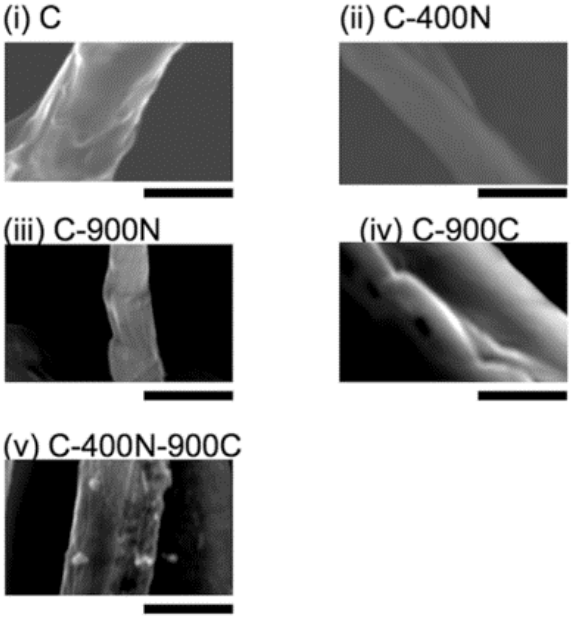


(a) (b)

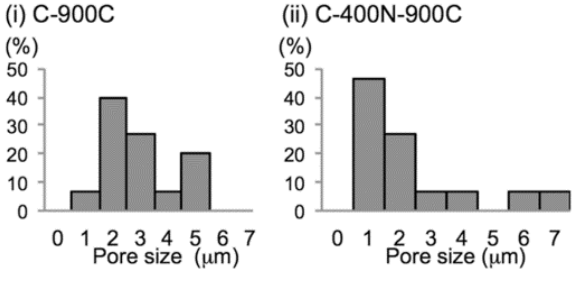
3.4 Pore sizes of ACFs

The properties of the pores on the surfaces of the fibres obtained under each heat-treatment condition were also of interest because pore size is strongly related to the adsorption functionality of the fibres (Kaewprasit et al., 1998). Therefore, the pore structures on the fibres in different samples were characterised via SEM at a three thousand magnification that enabled observation of each fibre [Figure 3(a)]. More than 30 fibres were observed for each sample. Notably, pore structures were detected only for C-900C and C-400N-900C [Figures 3(a)(iv) and 3(a)(v)]. The sizes of more than 30 pores in each of these two samples were then determined; the pore size distributions are shown in [Figure 3(b)]. For C-900C, the pore sizes were 1–5 μm [Figure 3(b)(i)], whereas most pore sizes for C-400N-900C were 1–4 μm, with a few larger pores [Figure 3(b)(ii)]. These results indicate that smaller pores are formed via two-step thermal treatment. Jain et al. (2013) reported on the distribution of pore sizes in activated carbon and investigated the relation between pore size and electrical function of activated carbon for use in capacitors (Yoda et al., 2017). The pore size data obtained herein would be beneficial for determining such a relation.

Figure 3 SEM images of the surfaces of ACFs prepared under different activation conditions and their pore size distributions, (a) typical SEM images: (i) Cotton (C), (ii) C-400N, (iii) C-900N, (iv) C-900C and (v) C-400N-900C. Scale bars indicate 10 μm (b) pore size distributions: (i) C-900C and (ii) C-400N-900C



(a)



(b)

3.5 Effect of two-step thermal treatment using carbon dioxide

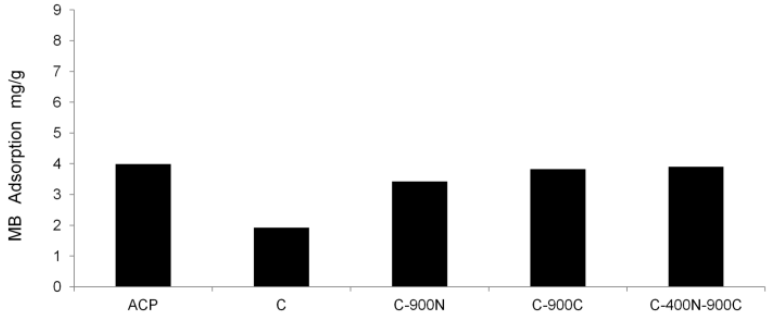
Generally, thermal degradation of carbon fibres occurs at 160°C–400°C and carbonisation and pyrolysis occur at 260°C–800°C (Ioannidou and Zabaniotou, 2007). A two-step thermal treatment process was expected to outperform a one-step treatment because each step in the two-step thermal treatment could be performed without mixing the gases. In addition, heating the cotton twice from room temperature to 400°C results in twice the thermal damage to generate the pore structure at 400°C as would be achieved by heating once to 900°C. Furthermore, the sample heat-treated in advance was planar, whereas that prepared in the tubular furnace was produced in a tubular state [Figure 1(a)]. We believe these factors enhanced the state of the pores on the surfaces of the generated

ACFs. Activated carbon with smaller pores exhibits better adsorption performance in an electric capacitor (Yoda et al., 2017). Therefore, this two-step thermal treatment is efficient for preparing ACF for use in capacitors. Previously, we explored the use of ACFs prepared from waste cloth and cloth manufacturing wastes in water filters and electric capacitors (Myoubudani et al., 2014, 2015). Based on the results, we anticipate that ACFs can be prepared from mixtures of different types of fibre products, including actual industrial waste fibres generated during the production of cloth and/or fibre.

3.6 Effect of two-step thermal treatment using carbon dioxide to enhance adsorption

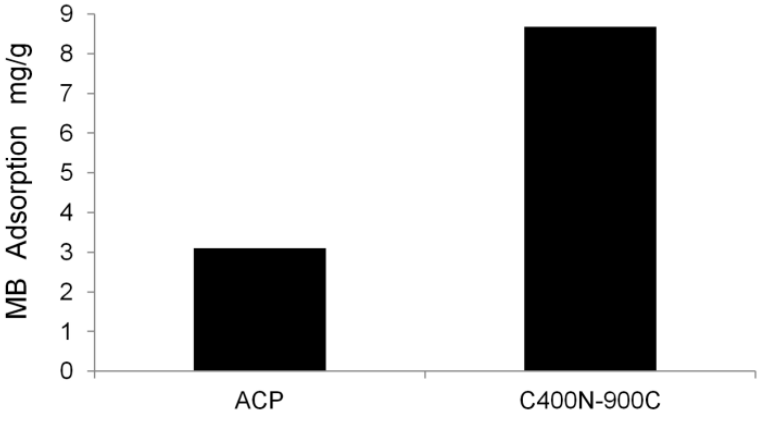
MB was used herein because of its strong adsorption onto materials and its usefulness in characterising activated carbons (Kaewprasit et al., 1998; Japanese Industrial Standards, 2014). First, we added 0.15 g of each type of fibre into MB solution (24 mg/L). ACP was used as a positive control. The typical adsorption isotherms of MB on ACP, C, C-900N, C-900C and C400N-900C are shown in Figure 4. Adsorption by ACP was almost identical to adsorption by C-900N, C-900C and C-400N-900C (Figure 4). Adsorption of MB on C-900C and on C-400N-900C was stronger than on C-900N (Figure 4). Results show that activation by carbon dioxide increased the adsorption. MB was most strongly adsorbed by C-400N-900C, demonstrating that the two-step thermal treatment is efficient for preparing adsorbing ACF.

Figure 4 Adsorption of MB onto fibres ACP, C, C-900N, C-900C and C-400-900C under conditions of 24 mg/L MB and 0.15 g fibre



The adsorption ability of C-400N-900C was further investigated by slightly changing the experimental conditions using 120 mg/L of MB and 1 g of C-400N-900C or ACP. Results are shown in Figure 5. ACF C-400N-900C adsorbed MB approximately three times more strongly than ACP, representing a dramatic increase. The substantial adsorption under these changed conditions indicates that the generated pore size is well suited for adsorption, with the pores covering a large surface area. This result also suggests that the two-step thermal treatment method can be used to prepare ACFs for electric capacitor applications because ACFs with smaller pores perform better when used in electric capacitors.

Figure 5 Adsorption of MB onto fibres ACP and C-400N-900C under conditions of 120 mg/L of MB and 1 g of fibre



4 Conclusions

We successfully prepared and characterised ACFs prepared from cotton using several heat-treatment processes. The diameters and width distributions of the ACFs were evaluated using SEM. In addition, pores were detected on the surfaces of those ACFs obtained from cotton activated using carbon dioxide. Results of the adsorption experiments revealed that the two-step thermal treatment is suitable for ACF preparation. Furthermore, the two-step thermal treatment was found to be the best method among those tested for the formation of thicker fibres with smaller pore structures, which would have the greatest potential for practical applications. Notably, this method may be readily used on other fibre products or industrial waste materials generated during the manufacture of cloth and fibres, thus enabling novel energy-storage solutions.

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