THE COMPARISON OF DIFFERENT ACTIVATION TECHNIQUES TO PREPARE ACTIVATED CARBON MATERIALS FROM WASTE COTTON FABRIC

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1. Introduction

Activated carbon (AC) has been widely used as a versatile adsorbent for separation of gases, removal of organic pollutants, and so on because of its large specific surface area, porous structure, and good adsorption properties [1-5]. Numerous researchers have studied on the preparation of carbon adsorbents with high surface area for adsorption and separation of gas. There are two methods for manufacturing ACs: physical and chemical activation [6]. Physical activation involves carbonization of the raw material in an inert atmosphere followed by mild oxidation of the raw material. Chemical activation involves impregnation of the raw material with dehydrating chemical agents including phosphoric acid, sulfuric acid, potassium hydroxide, and zinc chloride in an inert atmosphere [7,8]. The common feature of these impregnations leads to an increase in carbonization ability and, therefore, the development of a desired pore structure.

As waste cotton fiber is composed of cellulose—which have only three element (C, H, and O) and a higher carbon content (about 44%), it may be a potential substitute material for precursor to produce carbon materials. For example, Mustafa Özdemir [9] and Djordjevic [10] prepared ACs from cotton stalks or fibers by chemical activation with ZnCl₂ and H₂SO₄ and physical activation using CO₂. But H₂SO₄ is not environmentally sustainable solutions, and the two activation agents (ZnCl₂ and CO₂) used were more complex and expensive.

In this paper, we focus on the utilization of waste cotton fabric as raw materials for the preparation of ACs by applying one-step or two-step process of pyrolysis that use ZnCl₂ as activation agent. We study the difference between the two methods used for the preparation of ACs and the structure and properties of the waste cotton fiber–based carbon materials.

2. Material and methods

2.1. Raw materials

The waste cotton fabrics were collected from a local clothing factory in Taiyuan, Shanxi. ZnCl₂ with 99.9% purity was purchased from Nanjing Shuguang Chemical Group Co., Ltd. (Nanjing, China). BC-GR (purity of 99%, molecular formula is C₁₀H₁₄N₂Na₂O₇S₂; M.Wt = 556.49, C.I. Acid Red 73) was obtained from Qingdao Chuanlin Dye Industry Co., Ltd, China. CR-GL (purity of 92%, molecular formula is C₁₉H₁₇N₄S.Cl; M.Wt = 368.88, C.I. Basic Red 29) was obtained from Shanghai Runsoil Chemical Co., Ltd, China.

2.2. Preparation of the activated carbons (AC-WF)

In the one-step process, the waste cotton fabric was first washed for several times using tap water to remove impurities and dried in an oven at 80°C for 12 h. Then it was cut into small pieces (0.5 cm²). About 5 g of cotton fabric (on a dry basis) was impregnated with 50 mL of ZnCl₂ solution (55%) for 24 h. Then, the mixture was dried at 105°C for 12 h in an hot air oven. The impregnated sample was placed in a stainless steel horizontal reactor (7 cm in diameter and 100 cm in length) and then heated to the activation temperature of 700°C for 1 h under nitrogen atmosphere (99.99%) flow (100 mL min⁻¹) at a heating rate of 10°C min⁻¹. It was cooled down to room temperature under nitrogen atmosphere and then 50 mL of 0.1M hydrochloric acid solution was added to the carbonized product and stirred for 30 min. This mixture was filtered and washed with hot distilled water for several times to remove residual chemicals and chlorine until the pH of the filtrate was around 7. The obtained product was dried at 105°C for 10 h, stored in glass bottle for characterization and adsorption processes, and named as AC-WF-I.

Abstract:

In this paper, we investigate on the preparation of waste cotton fabric–based activated carbons by different methods. Two different kinds of carbon materials are prepared from waste cotton fabric, the structure and properties were characterized using instrumental analyses such as scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR). It is revealed that the products prepared using one-step process are composed of macroporous carbon network, which looks like sponge-type morphology, and exhibit the high values of qₑₒ₉ (1,198 mg/g) and qₑₒ₉ (235.6 ml/g), showing their potential usage as adsorbent.

Keywords:

Activation techniques; activated carbon materials; waste cotton fibers

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The chemical activation with ZnCl$_2$ is a two-step process: pre-carbonization and activation-carbonization process. The first process is pre-carbonization. In this process, 5 g of cotton fabric (on a dry basis) was placed in a stainless steel horizontal reactor and then heated to the activation temperature of 450°C for 1 h under nitrogen atmosphere. This is followed by the carbonization process in which 50 mL of ZnCl$_2$ solution (55%) was added to 5 g of the pre-carbonized fabric materials and kept for 24 h. After that, the samples are activated at 700°C for 1 h under nitrogen atmosphere and then allowed to cool to room temperature and named as AC-WF-II.

2.3. Characterization of the activated carbons

The morphologies of the samples are obtained with a scanning electron microscopy (SEM) (TESCAN, MIRA3 LMH). The composition and structure are analyzed using powder X-ray diffraction (XRD, Rigaku D/max-2500 diffractometer with Cu Ka radiation) and Fourier transform infrared spectroscopy (FTIR) (Bruker Tensor 27 spectrometer in the range of 500–4,000 cm$^{-1}$ on sample pellets made with KBr).

2.4. The methylene blue (MB) and iodine value

The methylene blue (MB) capacity and iodine value are determined by China National Standards (GB/T12496.8-1999 and GB/T12496.10-1999) to examine the adsorption capability of the prepared ACs. Under the optimum conditions, the methylene blue and iodine values at every level of every factor are shown in Tables S1 and S2. The range analysis is aimed to clarify the significance levels of different influencing factors on the iodine and methylene blue adsorption characterization of the prepared ACs. Based on the result of range analysis, the most significant factor could be disclosed. Tables S1 and S2 summarize the statistics analysis of the effect of different factors on the iodine and methylene blue values of prepared ACs. The $k$ is the average of the sum of each level of factor values, and the range value (R) for each average is the difference between the maximal and minimal values of the three levels.

Based on the results of range analysis, the significance sequence of all the investigated influencing factors is lined. In the one-step process, for the iodine value, the order of significance levels is shown as follows: ratio of ZnCl$_2$/fabric, impregnation time, carbonization temperature, and carbonization time. In the meanwhile, for methylene blue value, the order is: ratio of ZnCl$_2$/Fabric, carbonization temperature, impregnation time, and carbonization temperature. Based on the factors, the optimum conditions for the one-step process are shown in Table 1.

In the two-step process, for the iodine value, the order of significance levels is shown as follows: ratio of ZnCl$_2$/carbonized fabric, carbonized fabric impregnation time, activation time, and activation temperature. In the meanwhile, for the methylene blue value, the order is: ratio of ZnCl$_2$/carbonized fabric, activation temperature, activation time, and carbonized fabric impregnation time. Based on the factors, the optimum conditions for the two-step process are shown in Table 1.

Under the optimum conditions, the methylene blue and iodine values of AC prepared by the one-step process are 235.6 mL/g and 1,198.6 mg/g, respectively. For the two-step process, these values are 65.9 mL/g and 465.8 mg/g, respectively. The

| Table 1. The adsorption capability comparison with different activation technology |
|-----------------------------------|-----------------------------------|
| **The optimum condition**         | **results**                       |
| **ZnCl$_2$/Fabric ratio**         | **Impregnation time/h**           | **Carbonization temperature/°C** | **Carbonization time/min** | **Iodine value/mg/g** | **Methylene blue value/mL/g** |
| One-step                          | 3                                 | 8                                 | 700                        | 30                     | 1198.6                       | 235.6                        |
| Two-step                          | 4                                 | 8                                 | 700                        | 80                     | 465.8                        | 65.9                         |

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one-step process exhibits better adsorption capability than the steam physical activation method.

3.2. Characterization of AC-WF

Figure 1 shows the SEM images of the prepared carbon materials by the two kinds of methods. SEM images of the pre-carbonation and activation-carbonation of two-step method are shown in Fig. 1a and b, respectively. The pre-carbonation samples (Fig. 1a) are composed of many irregular mass that exhibit rough surfaces with many small irregular fragments over the surface. The morphology of activation-carbonation samples (AC-WF-II, Fig. 1b) is similar to that of pre-carbonation samples, expect a few holes on the surface. When activating with one-step process, in the SEM images of the resulting sample c and d, many pores of various sizes in a honeycomb can be observed on the sample surface. Figure 1d is the cross-sectional SEM image of AC-WF-I and shows many uniformly distributed pores and some pores are link up with each other. The SEM images shown in Fig. 1(c,d) clearly reveal that the AC-WF-I prepared by one-step process is composed of macroporous network of interconnected porous carbon, which looks like sponge-type morphology. Hence, the AC prepared by the one-step activation method is expected to have a better adsorption capacity.

In the one-step process, the activating reagent ZnCl₂ has been dissolved in water and then mixed with the precursor. In this way, the hydration of the precursor is facilitated, and the swelling of the fibers allows for a better access of the reactant to the interior of the fibers, which forces the incorporation of the reactant to the interior of the fibers. Once the impregnation step is finished, carbonization is carried out at high temperature under a flow of nitrogen; many gas including H₂O, CH₄, and CO₂ were produced and carried away by N₂ air flow. And, at last, the resulting carbon is washed to eliminate the rest of the chemical. Hence, a number of pores were formed on the surface and interior of the fibers.

FTIR is carried out to analyze the composition of the samples. As shown in the FTIR spectrum (Fig. 2), the appearance of a few number of adsorption peaks in the spectrum of AC-WF-I and AC-WF-II suggested that the chemical structure was simple. The peak at 3439 cm⁻¹ reflects the –OH stretching vibration, the bands at 1625 cm⁻¹ and 1436 cm⁻¹ were the characteristic of stretching vibration of C=C, while the band at 1109 cm⁻¹ indicated the C–O stretching vibrations in alcohols, phenols, or ether or ester groups [13]. Therefore, the prepared materials are mainly composed of amorphous carbons with different oxygen-containing surface groups. These carbon–oxygen groups may exercise a profound effect on the surface properties of ACs and
thus influence their adsorption characteristics, that is, these groups could be the potential active sites for the interaction with the adsorbate.

3. 3 Adsorption performance studies

3.3.1 The methylene blue (MB) and iodine adsorbed values

The iodine value (mg of iodine adsorbed/g of carbon) and methylene blue value (ml of methylene blue adsorbed/g of carbon) are considered as a measure of adsorption capability of AC. Normally, \( q_{\text{iodine}} \) denotes the amount of micropore and \( q_{\text{mb}} \) denotes the amount of mesopore of AC. As for the two-step process, in which the cotton fabric is carbonized at the first stage and activated with \( \text{ZnCl}_2 \) at the subsequent stage, porous carbons with lower adsorption capacities for methylene blue and iodine could be obtained. Under the optimal preparation condition, the values of \( q_{\text{iodine}} \) and \( q_{\text{mb}} \) for the AC-WF-II samples are 465.8 mg/g and 65.9 ml/g, respectively. Particularly, by the one-step process, in which the cotton fabric is carbonized and activated at the same stage, the higher values of \( q_{\text{iodine}} \) (1198 mg/g) and \( q_{\text{mb}} \) (235.6 ml/g) can be obtained. Therefore, the one-step process exhibits the better adsorption capability than the two-step process with different preparation condition. The comparison of capability of the waste cotton fabric–based AC with the National Standard is shown in Table 2. From the results, we can observe that the iodine and the methylene blue values of the AC-WF-I prepared under the optimum condition are higher than those of the first-grade product specified in the National Standard.

3.3.2 Preliminary adsorption studies of PC-WF

Equilibrium time is one of the most important parameters in the design of economical wastewater treatment systems. Figure 4 represents the adsorption capacity of 0.2 g of AC-WF-I versus the contact time for varying initial concentrations of dye between 250, 350, and 450 mg/L. The adsorption is initially (contact time<15 min) fast and then slows; the equilibrium was attained in about 120 min. The fast adsorption at the initial stage was probably due to the great concentration gradient between the dye in solution and the dye in the AC-WF-I because there must be a number of vacant sites available at the beginning. The progressive increase in adsorption and, consequently, the attainment of equilibrium adsorption are initially due to the limited mass transfer of the dye molecules from the bulk solution to the external surface of the adsorbent and are subsequently due to the slower internal mass transfer within the adsorbent particles [11,12]. As seen in Fig. 3, the amount of dye adsorbed

| Project                  | Main index                                      |
|--------------------------|-------------------------------------------------|
|                          | GB/T13803-1999                                  |
|                          | First-grade product | Second-grade product |
| Methylene blue value (ml/g) | 90 | 70 |
| Iodine value(mg/g)       | 1000 | 900 |
| One-step technology      | 235.6 | 65.9 |
| two-step technology      | 1198.6 | 465.8 |
increased evidently from 174.5 to 319.8 mg/g for BC-GR and from 499.5 to 842.5 mg/g for CR-GL with the increase in the initial concentration from 250 to 450 mg/L.

4. Conclusions

Two kinds of waste cotton fiber–based ACs are prepared by chemical activation with ZnCl₂ with different carbonization and activation methods. The optimum conditions are obtained respectively. The characterization results reveal that one-step process is better than the two-step process with respect to the porosity development. Therefore, the carbon products obtained by using one-step method exhibit high values of \( q_{\text{atm}} \) (1,198 mg/g) and \( q_{\text{mb}} \) (235.6 ml/g). Therefore, they can be used as low-cost adsorbent and considered as an alternative to the commercial AC.

The carbonization method described in this work is a facile, one-step, efficient, economic, and environmentally benign synthesis strategy to produce porous carbons, which can greatly cater for the global energy, resources, and environmental problems. Thus, this method is promising for the large-scale recycling of waste cotton textiles.

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Reference:

[1] Ahmad A.L., Loh M. M., Aziz J. A. (2007). Preparation and characterization of activated carbon from oil palm wood and its evaluation on methylene blue adsorption. Dyes and Pigments, 75, 263–272.

[2] Fukuyama H., Terai S. (2008). Preparing and characterizing the active carbon produced by steam and carbon dioxide as a heavy oil hydrocracking catalyst support, Catalysis Today, 130, 382–388.

[3] Ariyadejwanich P., Tanthapanichakoon W., Nakagawa K., Mukai S.R., Tamon H. (2003). Preparation and characterization of mesoporous activated carbon from waste tires. Carbon, 41, 157–164.

[4] Lee W.H., Reucroft P.J. (1999). Vapor adsorption on coal- and wood-based chemically activated carbons (II) adsorption of organic vapors, Carbon, 37, 15–20.

[5] Suzuki R.M., Andrade A.D., Sousa J.C., Rollemberg M.C. (2007). Preparation and characterization of activated carbon from rice bran. Bioresource Technology, 98, 1985–1991.

[6] Ahmadpour A., Do D.D. (1996). The preparation of active carbons from coal by chemical and physical activation. Carbon, 34, 471-479.

[7] Tomków K., Siemieniewska T., Czechowski F., Jankowska A. (1977). Formation of porous structures in activated brown-coal chars using \( O_2 \), \( CO_2 \), and \( H_2O \) as activating agents. Fuel, 56, 121-124.

[8] Fierro V., Torne-´Fernandez V., Celzard A. (2007). Highly microporous carbons prepared by activation of kraft lignin with KOH. Studies in Surface Science and Catalysis, 160, 607-614.

[9] Özdemir M., Bolgaz T., Saka C., Sahin Ö. (2011). Preparation and characterization of activated carbon from cotton stalks in a two-stage process. Journal of Analytical and Applied Pyrolysis, 92, 171-175.

[10] Djordjevic N., Djordjevic D., Miljkovic M., Urosevic S. (2014). Activated carbon from cotton waste as an adsorbent in the purification process of azo-dyes. Bulgarian Chemical Communications, 46, 277-282.

[11] González J.C., Sepúlveda-Escribano A., Molina-Sabio M., Rodríguez-Reinoso F., Mays T.J., et al. (1997). Characterization of Porous Solids. The Royal Society of Chemistry, Cambridge, 4, 9–16.
[11] Yao Y., He B., Xu F., Chen X. (2011). Equilibrium and kinetic studies of methyl orange adsorption on multi walled carbon nanotubes. Chemical engineering, 170(1), 82-89.

[12] Behera S.K., Kim J.H., Guo X., Park H.S. (2008). Adsorption equilibrium and kinetics of polyvinyl alcohol from aqueous solution on powdered activated carbon. Journal of hazardous material, 153(3), 1207-1214.

[13] Li T., Shen J.F., Li N., Ye M.G. (2012). Facile and novel hydrothermal preparation of functionalised carbon microspheres from glucose by using graphene sheets as a substrate. Materials Letters, 89, 202–205.

[12] Song M., Jin B.S., Xiao R., Yang L., Wu Y.M., Zhong Z.P., Huang Yaj. (2013). The comparison of two activation techniques to prepare activated carbon from corn. Biomass and Bioenergy, 48, 250–256.
Table S1. Methods of range analysis in orthogonal experiment of ZnCl₂ two-step activation method.

| Factor | A: ZnCl₂/Carbonized Fabric ratio | B: Carbonized Fabric impregnation time/h | C: Activation temperature °C | D: Activation time min | Results: Iodine value /mg/g | Results: Methylene blue value /mL/g |
|--------|----------------------------------|----------------------------------------|-----------------------------|------------------------|-----------------------------|---------------------------------|
| Sample |                                  |                                        |                             |                        |                             |                                 |
| 1      | 2                                | 4                                      | 500                         | 40                     | 52.8                        | 27.7                            |
| 2      | 2                                | 8                                      | 600                         | 60                     | 142.0                       | 10.3                            |
| 3      | 2                                | 12                                     | 700                         | 80                     | 277.4                       | 12.3                            |
| 4      | 3                                | 4                                      | 600                         | 80                     | 384.4                       | 20.8                            |
| 5      | 3                                | 8                                      | 700                         | 40                     | 382.6                       | 18.5                            |
| 6      | 3                                | 12                                     | 500                         | 60                     | 467.2                       | 19.9                            |
| 7      | 4                                | 4                                      | 700                         | 60                     | 445.0                       | 27.2                            |
| 8      | 4                                | 8                                      | 500                         | 80                     | 450.2                       | 44.5                            |
| 9      | 4                                | 12                                     | 600                         | 40                     | 506.4                       | 25.2                            |
| Iodine value |                                  |                                        |                             |                        |                             |                                 |
| k₁     | 157.4                            | 294.1                                  | 323.4                       | 314                    |                             |                                 |
| k₂     | 411.4                            | 324.9                                  | 344.3                       | 351.4                  |                             |                                 |
| k₃     | 467.2                            | 417.0                                  | 368.3                       | 370.7                  |                             |                                 |
| R      | 309.8                            | 122.9                                  | 44.9                        | 56.7                   |                             |                                 |
| Optimum scheme | A₃                         | B₂                                      | C₃                          | D₃                     |                             |                                 |
| Methylene blue value |                                  |                                        |                             |                        |                             |                                 |
| k₁     | 16.8                             | 25.2                                    | 30.7                        | 23.9                   |                             |                                 |
| k₂     | 19.7                             | 24.4                                    | 18.8                        | 19.1                   |                             |                                 |
| k₃     | 32.4                             | 19.2                                    | 19.3                        | 25.8                   |                             |                                 |
| R      | 15.6                             | 6.0                                     | 11.9                        | 6.7                    |                             |                                 |
| Optimum scheme | A₃                         | B₁                                      | C₁                          | D₃                     |                             |                                 |
Table S2. Methods of range analysis in orthogonal experiment of ZnCl₂ one-step activation method.

| Sample | Factor | A       | B       | C       | D       | Results       |
|--------|--------|---------|---------|---------|---------|---------------|
|        | ZnCl₂/Fabric ratio | Fabric impregnation time/h | Carbonation temperature /°C | Carbonation time/min | Iodine value / mg/g | Methylene blue value / mL/g |
| 1      | 2      | 8       | 500     | 30      | 1011.0  | 210           |
| 2      | 2      | 16      | 600     | 60      | 1155.7  | 130           |
| 3      | 2      | 24      | 700     | 90      | 1132.8  | 175           |
| 4      | 3      | 8       | 600     | 90      | 1178.6  | 230           |
| 5      | 3      | 16      | 700     | 30      | 1193.8  | 250           |
| 6      | 3      | 24      | 500     | 60      | 1168.1  | 170           |
| 7      | 4      | 8       | 700     | 60      | 1117.6  | 150           |
| 8      | 4      | 16      | 500     | 90      | 1148.1  | 155           |
| 9      | 4      | 24      | 600     | 30      | 1163.3  | 160           |

| Iodine value | \( k_1 \) | 1099.8 | 1102.4 | 1109.1 | 1122.7 |
|--------------|-----------|--------|--------|--------|--------|
| \( k_2 \)   | 1180.2    |        | 1165.9 | 1165.9 | 1147.1 |
| \( k_3 \)   | 1143.0    | 1154.7 | 1148.1 | 1153.2 |
| \( R \)     | 80.4      | 63.5   | 56.8   | 30.5   |
| Optimum scheme | \( A_2 \) | \( B_2 \) | \( C_2 \) | \( D_3 \) |

| Methylene blue value | \( k_1 \) | 172 | 197 | 178 | 207 |
|----------------------|-----------|-----|-----|-----|-----|
| \( k_2 \)           | 217       | 178 | 173 | 150 |
| \( k_3 \)           | 155       | 168 | 192 | 187 |
| \( R \)             | 62        | 29  | 19  | 57  |
| Optimum scheme      | \( A_2 \) | \( B_1 \) | \( C_3 \) | \( D_1 \) |