Adsorption for Dyes on Activation Carbons from Japanese Cedar Wood Prepared by Precarbonization and Two-stage Composite Activations with Wood Ash and Steam

Chia-Wen Peng and Han Chien Lin

Abstract—To prepare activated carbons (ACs) with higher BET specific surface area (S_{BET}) and revealed granulated particles with higher dye adsorption, Japanese cedar (*Cryptomeria japonica*) ash was used as a natural activating agent and also a precursor for preparing ACs using precarbonization and subsequent combined two-stage of activations with wood ash and steam. The yield and iodine value of the prepared ACs were 9.1-21.3% and 502.4-1171.1 mg/g. When the activation temperature was 750°C, the S_{BET} was 1619-1758 m^2/g and the micropore volume (V_{mi}) was 0.26-0.33 cm^3/g, which were higher than that activated by K_2CO_3 (S_{BET} 1537 m^2/g and V_{mi} 0.16 cm^3/g), and the required activation temperature was lower than the K_2CO_3 activation. Granular ACs (P200-0.25-750) at the yield of 14.9% and S_{BET} 1619 m^2/g could be prepared under the conditions of precarbonization temperature of 200°C, ash to water ratio of 0.25 wt%, activation temperature of 750°C, steam flow of 0.5 mL/min, and activation duration of 1.0 h, where the nitrogen adsorption-desorption isotherm type was Type IV, indicating the presence of micro/mesoporous structures mostly. The adsorbability of P200-0.25-750 for basic dye Auramine-O and Malachite green dye had simultaneous physical adsorption and ion exchange mechanisms, and in solutions onto prepared granular ACs were fitted with the Langmuir model with maximum adsorption capacity of 625.0 and 769.2 mg/g.

Index Terms—Activated carbons (ACs), precarbonization, wood ash, dye.

I. INTRODUCTION

The activation methods for preparing activated carbons (ACs) can be divided into physical and chemical activation methods; physical activation carbonizes the precursor, and uses the activated gas for activation at high temperature [1]-[3]; chemical activation uses a chemical activating agent to dehydrate and oxidize the precursor, and simultaneously proceeds with carbonization and activation at a low temperature. The activating agents are mostly strong acid, strong base, or alkali earth containing metallics; some can erode, melt, or dehydrate the precursor and equipment, while some perform oxidation. The chemical activation method requires lower activation temperature and shorter activation duration than physical activation, and has better pore structure development of the prepared ACs and higher yield [2]-[4]; however, the chemical residues after activation pollute the environment, produce the eutrophication, and chemical activating agent remains in the ACs [5], [6], thus, it is urgent to develop natural material-based and environmentally friendly activating agent.

Wood pellets in renewable energy can be permanently used, and because the CO_2 released from combustion is photosynthesized by plants and fixed by plants, as well as the advantage is carbon neutral. The global yield of wood pellets was 22 million MT in 2013 [7]; however, wood ash increases with consumption, is mostly regarded as waste at present, and must be buried at a high cost [8]-[10]. Wood ash is strong base (pH > 13) and alkali metal containing salts, oxide, hydroxide, or carbonate [11], [12], and arbitrary discarding can pollute the environment and rivers. As it is difficult to find appropriate landfill sites and environmental laws have become increasingly strict, disposal costs will be higher [10]. Therefore, in order to implement waste reduction and waste recycling principles, it is necessary to recover wood ash for better purposes. According to Marsh and Rodríguez-Reinoso (2006) [13], regarding the mechanism for preparing ACs by alkali salt activation, the oxygen atoms of hydrogen-oxygen mixture, sodium carbonate, or potassium carbonate gasify carbon atoms to generate CO and pores. This gasification is catalyzed by alkali salt, and the alkali salt is reduced by carbon, thus, producing Na or K metal atoms, which are embedded in the carbon structure, in order to expand the carbon lattice [14]-[19].

About 128 MT of residual dyes are discharged globally into the environment per day, which pollutes water [20], may be directly poisonous and carcinogenic to the human body through the food chain, is hazardous to aquatic life [21]-[24], influences the light penetration ability of water, and degrades the self-purification capacity of rivers [25]. According to the Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry investigation of 4,000 kinds of dyes on the market, the half lethal dose value of over 90% of them is 2×10^3 mg/kg, where basic dyes and diazo direct dyes have the highest toxicity [26], [27]. In addition, there are more than 100 thousand kinds of dyes on the global market, where the total output is as high as 700 thousand MT/year [22], [28]-[30], as dyes are universally used in many industries, such as textile, paper-making, leather, food, printing,

Chia-Wen Peng is with the Experimental Forest, College of Bio-Resources and Agriculture, National Taiwan University, Nantou, Taiwan (e-mail: s0981490@alumni.ncyu.edu.tw).

Han Chien Lin is with the Department of Wood Based Materials and Design, National Chiayi University, 60004 Chiayi, Taiwan (e-mail: alexhlin@mail.ncyu.edu.tw).

cosmetics, pharmacy, and plastics [22], [23], [30], [31]. The paper industry is the second largest user of dyes in the U.S., where ordinary colored paper accounts for 40%, primary pulp paper accounts for 20%, color card paper accounts for 20%, and medical paper accounts for 10%. The dyeing process produces a great deal of waste water, which contain residual dyes, and even if there is only a trace amount (< 1 ppm) of residue, it is still visible and discomforting [22], [27], [32]. The basic dyes of the paper industry are mostly diphenylmethane or triphenylmethane, which have organism safety issues according to animal experiments, such as carcinogenicity, mutagenicity, and teratogenicity [33]. Therefore, industrial waste waters with dyes should be treated to meet discharge standards before being discharged into the environment. There have been multiple methods for removing dyes from wastewater, and ACs adsorption have high specific surface area, large adsorption volume, rapid adsorption dynamics, and relatively easy regeneration [34], thus, they can rapidly reduce the concentration of dyes in water [30], [31], [35], are applicable to various dyes [27], and are readily available and easily used [36], [37]. While they are more expensive than other adsorbents, they have good effectiveness, and are one of the key points of the present dye wastewater pollution prevention engineering.

While wood ash activation can promote the formation of ACs pores [38]-[40], the pore structure of the prepared ACs is mostly micropores, which is disadvantage to adsorbing large molecules in the liquid phase, such as dyes, humic acid, or vitamins [41]. Peng *et al.* (2013) [42] indicates that using physical/chemical or composite activations to prepare ACs after the precursor is precarbonized can increase the BET specific surface area of ACs, promote pore development, enhance adsorbability, and form granular shapes. Therefore, in order to prepare granular ACs with higher specific surface area and higher adsorbability for dye, this study used Japanese cedar (*Cryptomeria japonica*) ash as the natural activating agent and the precursor to prepare ACs using two-stage composite of activations with wood ash and steam after precarbonization. The effect of precarbonization temperature and activation temperature on the characterization of ACs was investigated. The prepared ACs, as prepared under the optimal preparation conditions, was to incestigate the adsorbability for basic Auramine-O and Malachite green dyes. The specific surface area, pore characterization, and dye adsorbability were compared with that of the ACs prepared by chemical activator potassium carbonate [19], [43]-[47]. The Langmuir and Freundlich adsorption isotherms were used to evaluate the analysis of optimal isotherm. The results are expected to provide reference for preparing ACs through the activation of wood ash from the combustion of wood pellets, and use them to adsorb dyes in the future, in order to recycle waste wood ash and enhance the Cascade type and sustainable utilization of forest resources.

II. MATERIALS AND METHODES

A. Materials

Japanese cedar (*Cryptomeria japonica* D. Don) thinning wood was debarked, sliced, and pulverized, and 20-40 mesh particles [48] were screened through a screen mesh as the precursor for precarbonization. Japanese cedar wood ash and distilled water were mixed. The ash to water ratio of 0.25 wt% was used as the natural activating agent [38], [40]. The specimen of ACs for industrial waste water, code COM-AC, as bought from Taiwan Active Carbon. Two types of basic dye Auramine-O (BY2) and Malachite green (BG4) of the paper industry were used as adsorbate [23], [49], as bought from Merck Taiwan with test analysis level.

B. Preparation of ACs

About 150 g of precursor Japanese cedar particles were placed on a stainless steel disc in a vertical high temperature activation furnace (inner diameter, 26 cm; inner height, 40 cm; Chi-How Heating Co., Ltd.), nitrogen was imported for precarbonization after vacuum pumping, the temperatures were set as 200, 300, 400, and 500°C, respectively [50]-[52], the heating rate was 10 °C/min, and the final precarbonization temperature was maintained for 1.0 h [42]. Finally, the furnace was cooled to room temperature by circulating nitrogen, and the prepared precarbonized specimen was used for preparing ACs.

For two-stage composite activations with wood ash and steam, the prepared precarbonized specimen was dipped in wood ash (ash to water ratio 0.25 wt%) for 24 h [38], [39], filtered and dried at 103±2 °C till absolutely dry, and then, about 10 g was placed in a square crucible, which is placed in the vertical high temperature activation furnace, and the nitrogen was imported for activation after vacuum pumping. The activation temperatures are set as 550, 650, and 750 °C, respectively, the heating rate was 10°C /min, when the preset activation temperature was reached, the nitrogen input was stopped, the steam was imported for activation, and the flow was set as 0.5 mL/min [42], [53], [54]. After 1.0 h activation, it was cooled to room temperature by circulating nitrogen. The test specimen codes are P200-500 (pre-carbonization temperature) -0.25 (ash to water ratio) -550, 650, 750 (activation temperature).

For Potassium carbonate activation, the ACs was prepared using chemical activating agent K_2CO_3, as in [16], [17], [45], [46], [55]. The K_2CO_3 and Japanese cedar particles had an impregnation ratio of 1.0 wt% and distilled water at weight ratio of 1:1:1.3, which were thoroughly mixed [56], and dried at 103±2 °C for 24 h. The ACs was prepared under the conditions of an activation temperature of 800°C, heating rate of 10°C /min, and activation time of 1 h. The testing code for the specimen: K_2CO_3 (potassium carbonate activation) -1.00 (impregnation ratio) -800 (activation temperature).

C. Measurement of ACs Characterization

Measurement of yield, iodine value, BET specific surface area, and pore characterization [38], [40] of ACs was performed. The particle size and distribution of ACs were measured by a laser diffraction size distribution analyzer (MALVERN, Mastersizer 2000), as in [39]. The zeta potential (ξ-potential, ±150 mV) of the prepared ACs was measured by a dynamic light scattering analyzer (MALVERN, Nano-ZS).

D. Dye Adsorption/Desorption Performance Measurement

The BY2 and BG4 dye solutions were prepared, their

absorption spectra were measured by spectrophotometer (Dynamica, HALO RB-10), and the wavelength of the maximum absorbance value was selected as the detection wavelength [23], where the λ_{max} of BY2 and BG4 are 432 and 618 nm, respectively. The adsorbates at different concentrations were prepared, the initial concentration range of the dye solution was 50-1000mg/L, 100mL of the dye solution was poured into a 250 mL conical flask each time, mixed with 0.1 g ACs, vibrated at speed of 130 rpm and $28\pm1^{o}C$ in the shaker for 5 days, filtered through a glass fiber filter (pore size 0.5 μm) after reaching adsorption equilibrium, and the concentration of adsorbate in the solution was measured by spectrophotometer. The isothermal equilibrium adsorbance q_e computing equation (1) is expressed, as follows:

$$q_e = \frac{(C_0 - C_e)}{W} \bullet V$$

(1)

where C_0 and C_e are the initial and equilibrium concentrations (mg/L), respectively, V is the volume of liquid (L), and W is the ACs weight (g).

Langmuir and Freundlich isotherms are used for analysis. The Langmuir isotherm assumes monolayer adsorption on an even surface, and is the theoretical model of monolayer adsorption, expressed as Equation (2):

$$C_e/q_e = (1/K_L q_{mon}) + (1/q_{mon}) C_e$$

(2)

where C_e: liquid-phase concentration after equilibrium, q_e: adsorbance (mg/g) of the adsorbent during equilibrium, q_{mon}: adsorbance of a single-layer covering, K_L: Langmuir constant, the C_e is drawn by C_e/q_e according to Equation (1), and K_L and q_{mon} are obtained by calculating intercept ($1/K_L q_{mon}$) and slope ($1/q_{mon}$).

The Freundlich isotherm is suitable for describing atypical adsorption on a non-uniform surface. The nonuniformity is resulted from the interaction between different surface functional groups and adsorbent and adsorbate [49], is used for surface nonuniform adsorbent, isothermal adsorption for single solute system in a concentration range, expressed as Equation (3):

$$\log q_e = \log K_F + (1/n) \log C$$

(3)

where C_e: liquid-phase concentration after equilibrium, q_e: adsorbance of adsorbent during equilibrium, K_F is a constant, and n represents the adsorption strength, as obtained by drawing log C_e from log q_e.

For measurement of the effect of pH value on ACs adsorption, the adsorbates (pH 3-9) of different pH values were prepared by 0.1 N NaOH and 0.1 N HCl [49] , the initial concentration of dye solution was 300 mg/L, 200 mL dye solution was poured into the 250 mL conical flask each time, mixed with 0.1 g ACs [57], vibrated at 140 rpm and the equilibrium temperature of $28\pm1^{o}C$ in the shaker for 26 h, and isothermal equilibrium adsorbance was obtained according to the aforesaid process after adsorption equilibrium (q_e, mg/g).

In dye desorption test the ACs specimen adsorbing BY2 and BG4 dyes (200 mg/L) was filtered through glass fiber filter paper, the filter paper and ACs after filtration were dried in a $70^{o}C$ oven for 24 h, and the dye adsorption quantity Q_e (mg) was obtained through the aforesaid process from the filtrate. Regarding the dye desorption of ACs, the eluent

de-ionized (DI) water, HCl (0.1 N), and NaOH (0.1 N) 50 mL were placed in the 250 mL conical flask, mixed with 50 mg dried ACs [58], [59], vibrated at the speed of 150 rpm and equilibrium temperature of $28\pm1^{o}C$ in the shaker for 24 h before filtration, and the dye desorption quantity Q_d (mg) is obtained through the aforesaid process from the filtrate. Each sample is tested three times, and the dye desorption rate (E_d) of ACs (4) is calculated, as follows [37]:

$$E_d = \frac{Q_d}{Q_e} \times 100\%$$

(4)

where Q_d: dye desorption quantity (mg); Q_e: dye adsorption quantity (mg)

E. Statistical Analysis

The results expressing mean and standard deviation were statistically analyzed by applying Duncan's multiple range tests at a 5% significance level ($\rho < 0.05$), using the Statistical Package for Social Science (SPSS 16.0) software.

TABLE I: YIELD AND IODINE VALUE OF ACs PREPARED WITH VARIOUS CONDITIONS

AC	Yield (%)	Iodine value (mg/g)
0.00-850 [1]	20.6 (0.2) [2]	770.5 (12.9)
0.25-750 [3]	13.1 (0.1)	1101.5 (7.2)
P200-0.25-550 [4]	21.3 (0.1)	502.4 (0.2)
P200-0.25-650	16.0 (0.1)	0861.8 (7.1)
P200-0.25-750	14.9 (0.2) [d 5)]	1155.2 (1.3) [c]
P300-0.25-750	11.2 (0.1) [c]	1171.1 (4.5) [d]
P400-0.25-750	10.1 (0.2) [b]	1135.0 (7.3) [b]
P500-0.25-750	9.1 (0.1) [a]	1097.3 (7.1) [a]
K$_2$CO$_3$-1.00-800	14.2 (0.4)	1151.2 (2.5)

[1] Activation with steam, Specimen code: ash to water ratio-activation temperature.
[2] Mean (standard deviation).
[3] Combining activations with wood ash and steam, Specimen code: ash to water ratio-activation temperature.
[4] Combining precarbonization and activations with wood ash and steam, Specimen code: precarbonization temperature-ash to water ratio-activation temperature.
[5] Mean (standard deviation), numbers followed by different letters are significantly different at the level of $\rho < 0.05$ according to Duncan's multiple range tests.

III. RESULTS AND DISCUSSION

A. Properties of the ACs

The ACs of the control group (0.00-850) was prepared by steam at an activation temperature of $850^{o}C$ for 1.0 h, the yield was 20.6%, and the iodine value was 770.5 mg/g. The yield and iodine value of the ACs prepared by two-stage composite activations with wood ash and steam at the activation temperature of 750 ^{o}C of another control group (0.25-750) were 13.1% and 1101.5 mg/g, respectively. The yield and iodine value of ACss prepared by using two-stage composite of activations with wood ash and steam after precarbonization were 9.1-21.3% and 502.4-1171.1 mg/g. The yield of the carbon activated at $750^{o}C$ decreased as the precarbonization temperature increased, according to Duncan's multiple range analysis results, and there was significant difference (Table I).

In terms of the effect of precarbonization temperature on the iodine value of ACs (P300-0.25-750), the

precarbonization temperature of 300°C results in the maximum iodine value of 1171.1 mg/g, and there was significant difference. The yield and iodine value of the ACs (K_2CO_3-1.00-800) prepared by chemical activation of K_2CO_3 were 14.2% and 1151.2 mg/g, respectively; while the yield was a little lower than that of P200-0.25-750, their iodine values were close to each other.

Table II showed S_{BET} 712 m^2/g, V_{tot} 0.36 cm^3/g, V_{mi}/V_{tot} 78.0%, and D 2.02 nm of 0.00-850. The S_{BET}, S_{ex} and V_{tot} of 0.25-750 were 1285 m^2/g, 544 m^2/g and 0.63 cm^3/g, respectively. The 0.25-750 is 1.8, 5.0, and 1.8 times that of the 0.00-850. However, the S_{BET}, S_{ex}, and V_{tot} of the precarbonization temperature of 200-500 °C and two-stage composite activations with wood ash and steam were 1619-1758 m^2/g, 922-1118 m^2/g, and 0.82-0.85 cm^3/g, respectively. The P300-0.25-750 had the highest S_{BET} (1758 m^2/g) and V_{tot} (0.85 cm^3/g) and high S_{ex} (1094 m^2/g), which were about 1.4, 2.0, and 1.4 times that of the 0.25-750. Therefore, the precarbonized precursor results in well organized and stable carbon structure, and the carbon layer end contains a few oxygen-containing functional groups [60]. As it can resist drastic gasification decomposition and prevent the carbon structure from breaking down during the activating reaction, micropores with high adsorbability can be formed [61]. According to Table I and Table II, the S_{BET}, S_{ex}, V_{tot} and iodine value of the ACs increased and then decreased as the precarbonization temperature increased. The P300-0.25-750 at the precarbonization temperature of 300 °C had the maximum BET specific surface area and iodine value, and high S_{ex}. However, when the precarbonization temperature increased to 500°C, the S_{BET}, S_{ex}, V_{tot} and iodine valur decreased to 1659 m^2/g, 922 m^2/g, 0.82 cm^3/g, and 1097.3 mg/g, respectively, meaning an appropriate precarbonization temperature contributes to pore development and enhances adsorbability.

TABLE II: POROSITY OF ACs PREPARED WITH VARIOUS CONDITIONS

AC	S_{BET} [1] (m^2/g)	S_{ex} [2] (m^2/g)	V_{mi} [3] (cm^3/g)	V_{tot} [4] (cm^3/g)	Vmi/Vtot (%)	D [5] (nm)
0.00-850 [6]	712	109	0.28	0.36	78.0	2.02
0.25-750 [7]	1285	544	0.34	0.63	53.6	1.97
P200-0.25-550 [8]	509	73	0.20	0.25	82.1	1.94
P200-0.25-650	1096	453	0.29	0.53	54.8	1.95
P200-0.25-750	1619	940	0.30	0.84	36.0	2.07
P300-0.25-750	1758	1094	0.29	0.85	34.2	1.94
P400-0.25-750	1708	1118	0.26	0.83	30.9	1.95
P500-0.25-750	1659	922	0.33	0.82	40.4	1.97
K_2CO_3-1.00-800	1537	1162	0.16	0.86	18.6	2.23

[1] S_{BET}: specific surface area; [2] S_{ex}: external surface area; [3] V_{mi}: micropore volume; [4] V_{tot}: total pore volume; [5] D: average diameter of pore; [6, 7 and 8] see Table I [1), 3) and 4)]

According to Table I, the yield decreased as the precarbonization temperature increased, and there was significant difference. The precarbonization temperature of 200°C was higher, thus, the precarbonization temperature of 200°C, two-stage composite activations with wood ash and steam, and different activation temperatures of P200-0.25-550/650/750 were used to discuss the BET specific surface area and pore characterization. The results showed that when the activation temperature increased from 550 to 750°C, the S_{BET} increased from 509 to 1619 m^2/g

(Table II), indicating S_{BET} increased with the activation temperature, and as the micropore walls collapse, the number of meso- or macrospores increased greatly, S_{ex} increased from 73 m^2/g to 940 m^2/g, V_{mi}/V_{tot} decreased from 82.1% to 36.0%, and D increased from 1.94 nm to 2.07 nm. In addition, when the activation temperature increased from 650 to 750 °C, V_{tot} increased greatly with the activation temperature, V_{mi} increased slightly, but S_{ex} increases greatly, thus, the micropores and mesopores are increased by activation [17]. According to the S_{BET} 1537 m^2/g and V_{tot} 0.860 cm^3/g of the ACs, as prepared by the chemical activation of K_2CO_3, the K compound is formed and diffused in the internal structure of the precursor carbon matrix during activation, which enlarges pores and forms new pores [17], [57], [62]. According to the pore characterization results [42], [63]-[66] of K_2CO_3-1.00-800 in this study and the wood/bamboo ACs are prepared by the composite activations with K_2CO_3 and steam, the S_{BET} and V_{tot} of various ACss are lower than this study. The S_{BET} of P200/300/400/500-0.25-750 in this study was 1619-1758 m^2/g and the V_{mi} was 0.26-0.33 cm^3/g, which was higher than the S_{BET} 1537 m^2/g and V_{mi} 0.16 cm^3/g of K_2CO_3; therefore, the required activation temperature was lower than K_2CO_3 activation.

B. Adsorption-desorption Isotherms

According to the nitrogen adsorption-desorption isotherms of ACs 0.25-750 (Fig. 1), the initial adsorptive value was only 272 cm^3/g, and there was an obvious delay wheel [46].
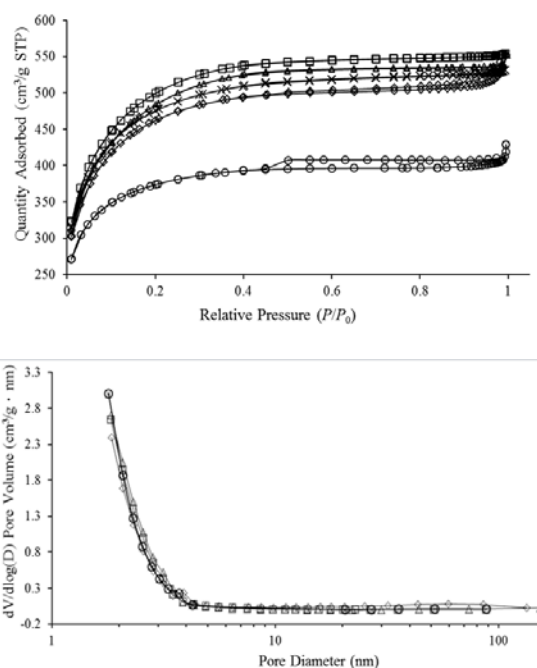

Fig. 1. Nitrogen adsorption-desorption isotherms and pore size distribution of ACs with different preparing conditions.
Legends: —◇— : P200-0.25-750, —□— : P300-0.25-750, —△— : P400-0.25-750, —✕— : P500-0.25-750, —○— :0.25-750
Note: Specimen code see Table I.

In accordance with the Brunauer, Deming, Deming, and Teller (BDDT) classified adsorption isotherm types, it is Type IV, meaning micropores and mostly mesopores. Hameed and Kl-Khaiary (2008) [49] indicate that an ACs surface has lost the original cell fiber morphology; as

mentioned above, a carbon structure without precarbonization is prone to rigorous gasification decomposition and breakdown during activation, meaning that it loses the original wood cell fiber morphology. The initial adsorptive value of P200/300/400/500-0.25-750 in Fig. 1 was 301-321 cm^3/g, and as the relative pressure P/P_0 increased, the adsorption volume rising slope was larger than 0.25-750, meaning pore size distribution was wide. In addition, as the nitrogen adsorption-desorption isotherms are plain shaped under high relative pressure, when the P/P_0 approaches saturation, the isotherm trailing increases sharply [18], [50], [67], thus, it can be regarded as the result of limited nitrogen adsorption, meaning the adsorbate implements capillary condensation in mesopores, namely, the proportion of mesopores of the ACs is increased.

C. Adsorption-desorption Isotherms

According to Fig. 2, the mean particle sizes of ACss 0.00-850, 0.25-750, P200-0.25-750, and K$_2$CO$_3$-1.00-800 were 130.7, 84.9, 94.6, and 32.8 μm, respectively. The K$_2$CO$_3$-1.00-800 had the minimum particle size as it was powdered, and is close to the mean particle size of general powdered ACs, which is 15-25 μm [1], and is identical to the result of the powdered ACs prepared from lignocelluloses' materials activated by a general chemical activating agent [44]. In addition, while the ACs prepared by 0.25-750 and P200-0.25-750 was granular, the mean particle size of P200-0.25-750 (94.6 μm) was larger than that of 0.25-750 (84.9 μm), and the particle size had another peak in the range of 1096.5-1258.9 μm. Therefore, the precarbonized precursor resulted in a well organized and stable carbon structure, which could resist rigorous gasification decomposition and prevented the carbon structure from breaking down during the activating reaction. Thus, the prepared ACs can maintain the original morphology [60], [61], namely, the ACs is mostly granular.
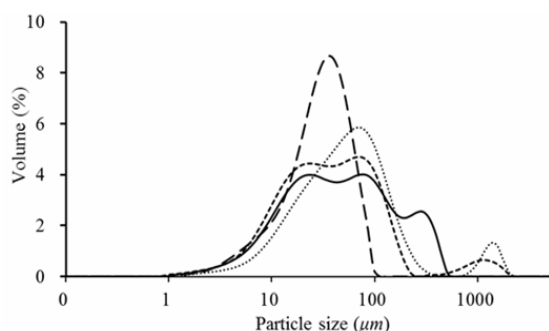

Fig. 2. Particle size and distribution of ACs with different preparing conditions.
Legends: ……:0.00-850, ——:0.25-750, ─ ─ ─ :P200-0.25-75
─ ─ ─ ─ 0:K$_2$CO$_3$-1.00-800

D. Zeta Potential

In a system with H$^+$, OH$^-$ and other ions, the chemical action on the surface, e.g. adsorption, makes the surface potential of the suspended particles neutral, thus, the pH value is called the point of zero charge (pH$_{PZC}$) [64]. When pH > pH$_{PZC}$, the acid functional group is separated, releasing protons, and leaving a negatively charged carbon surface, which is favorable for cation adsorption. On the contrary,

when pH < pH$_{PZC}$, the basic functional group bonds the protons, leaving a positively charged surface, which is favorable for anion adsorption [68]. This study selected P200-0.25-750 ACs under better preparation conditions in order to measure the zeta potential under pH 2, 4, 6, 8, and 10, and the results (not shown in Fig. 2) showed that, the zeta potential 10.9 mV was positive when the solution pH was 2, and the zeta potential was 0 mV when the solution pH was 3, meaning the zeta potential of P200-0.25-750 was in pH 3. However, the zeta potential was negative when solution was pH > 3, meaning the number of negatively charged active sites is increased, while the number of positively charged sites is reduced [23], [37]. When the solution pH value increased to pH 4, pH 6, pH 8, and pH 10, the pH$_{PZC}$ was -12.2, -36.2, -25.9, and -40.8 mV, respectively, and remained negative, meaning there were multiple negatively charged active sites on the surface of the ACs P200-0.25-750 in this pH range, which is favorable for adsorbing positively charged ions [69].

E. Dye Adsorption Isothermal Equilibrium of ACs

The adsorbent surface characterization and adsorption mechanism can be known from the adsorption isotherm and its parameters, which are often used to determine the interaction of adsorbent and adsorbate, in order to evaluate the suitability of the adsorbent. This study used P200-0.25-750 as the adsorbent for dye adsorption testing, and compared the adsorbability of the prepared ACss of 0.00-850, 0.25-750, and K$_2$CO$_3$-1.00-800 with that of commercial COM-AC for BY2 and BG4. According to Table 3, when the initial concentration of dye was 50-1000 mg/L, the adsorbance of various ACss for BY2 and BG4 was 222.2-625.0 mg/g and 312.5-769.2 mg/g, respectively. The P200-0.25-750 had the maximum adsorbance, which was 625.0 mg/g and 769.2 mg/g, respectively. The 0.00-850 had the minimum adsorbance, which was 222.2 mg/g and 312.5 mg/g, respectively. According to the results, the BY2 and BG4 dyes adsorption quantity increased with the S_{BET} and S_{ex} of ACss other than K$_2$CO$_3$-1.00-800 (Table II), because the developed mesopores' structure is connected to the micropore channel, which is favorable for the adsorption result of ACs [70]. However, the K$_2$CO$_3$-1.00-800 had high S_{BET} 1537 m^2/g and S_{ex} 1162 m^2/g, but less micropores (V_{mi} 0.16 cm^3/g, V_{mi}/V_{tot} 18.6%, Table II), meaning it is disadvantage to adsorbing micro-molecular adsorbate [21], [23], [37], [49], [71]-[75].

The results of the isothermal equilibrium parameter and r^2 of BY2 and BG4 dyes adsorbed by various ACss are also shown in Table III. The r^2 of Langmuir isotherm was 0.998-1.000 and 0.999-1.000, respectively, while the r^2 of Freundlich isotherm was 0.343-0.755 and 0.433-0.771, respectively. The Langmuir isotherm was more suitable than Freundlich isotherm (Fig. 3), and the adsorption of the two dyes on all ACss conformed to the Langmuir adsorption isotherm, meaning the dye molecules cover the external surface of ACs in single layer [76]. In addition, the basic feature of Langmuir adsorption isotherm can be regarded as a dimensionless constant (5), called the separation factor (R_L) [49], [77], and expressed, as follows:

$$R_L = \frac{1}{(1 + K_L \times C_0)} \qquad (5)$$

where: K_L: Langmuir adsorption constant (mg/L)
$\quad$ C_0: Maximum initial dye strength
$\quad$ $R_L > 1$ represents unfavorable adsorption
$\quad$ $0 < R_L < 1$ represents favorable adsorption
$\quad$ $R_L = 1$ represents linear adsorption

$R_L = 0$ represents irreversible adsorption reaction

According to the R_L values in Table III, the R_L values of BY2 and BG4 dyes adsorbed by various ACss were 0.0002-0.0031 and 0.0008-0.0031, respectively, which was favorable for adsorption, as it is 0-1.

TABLE III: PARAMETERS OF LANGMUIR AND FREUNDLICH EQUATION FOR BY2 AND BG4 DYE ADSORPTION IN VARIOUS ACs

Adsorbate	Adsorbent [1] (ACs)	Langmuir				Freundlich		
		q_{mon} [2] (mg/g)	K_L [3]	R_L [4]	r^2	K_F [5]	n [6]	r^2
BY2 [7]	0.00-850	222.2	1.36	0.0016	0.999	126.7	7.87	0.708
	0.25-750	555.6	0.36	0.0031	0.998	217.3	5.19	0.755
	P200-0.25-750	625.0	0.31	0.0028	0.998	242.3	5.99	0.565
	K$_2$CO$_3$-1.00-800	500.0	2.86	0.0004	1.000	247.0	7.26	0.343
	COM-AC [9]	303.0	5.50	0.0002	0.999	144.6	6.84	0.593
BG4 [8]	0.00-850	312.5	0.46	0.0031	1.000	106.9	4.33	0.771
	0.25-750	666.7	0.71	0.0016	0.999	214.8	3.62	0.641
	P200-0.25-750	769.2	0.72	0.0012	0.999	276.1	4.61	0.448
	K$_2$CO$_3$-1.00-800	454.5	1.29	0.0008	1.000	195.1	6.50	0.433
	COM-AC	555.6	0.50	0.0021	0.999	178.8	4.40	0.634

[1] See Table I; [2] q_{mon}: Adsorption capacities; [3] K_L: Langmuir constant; [4] R_L: Separation factor; [5] K_F: Freundlich constant; [6] n: Adsorption strength; [7] BY2: Auramine-O; [8] BG4: Malachite green; [9] COM-AC: Commercial ACs.
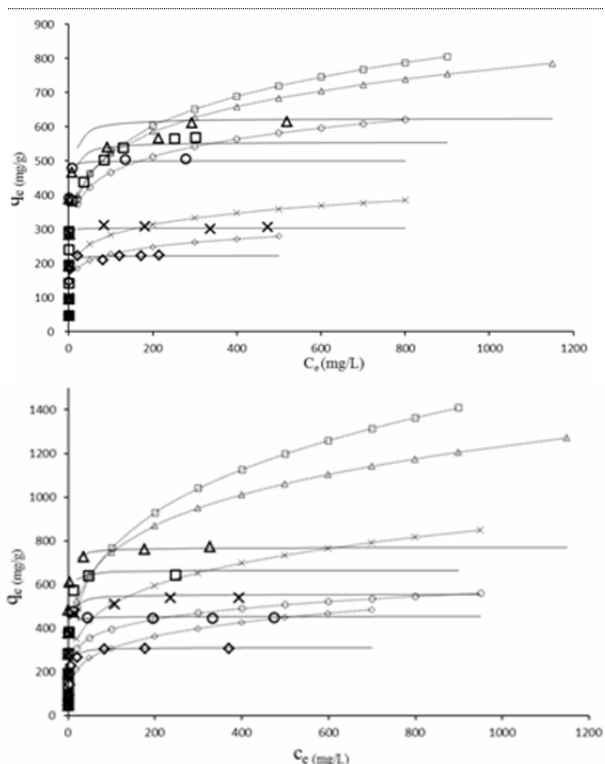

Fig. 3. Adsorption isotherms of BY2 (top figure) and BG4 (down figure) to ACs.
Legends: $\diamond$: 0.00-850, $\circ$: K$_2$CO$_3$-1.00-800,
$\times$: COM-AC, $\square$: 0.25-750, P200-0.25-750
——— : Langmuir isotherm, ——— : Freundlich isotherm

F. Effect of PH Value on ACs Adsorption

This study used ACs P200-0.25-750 under better preparation conditions to discuss the effect on adsorbing BY2 and BG4 dye liquors of different pH values, where the dye liquid pH value was set as 3-9 (not shown in Fig. 3). According to the results, when the pH value increased from 3 to 5, the adsorbance of BY2 and BG4 dyes increased from 276 mg/g to 320 mg/g and 295 mg/g, respectively, and increased to 336 mg/g. The adsorbance increased with pH value; as mentioned above, when the P200-0.25-750 was in a solution with pH 3-5, the zeta potential decreased from 0 to -23 mV, and it is inferred that the number of negatively

charged active sites is increased [23], [37], thus, it is favorable for adsorbing cationic dye molecules. The adsorption of BG4 dye on P200-0.25-750, and the adsorption of malachite green dye on scrap tire ACs were identical with the result of the pH < 5 solution, meaning the solution hydrogen ion concentration is high and occupies partial adsorption sites, which is unfavorable for adsorbing malachite green dye [75]. The adsorption of BY2 dye on P200-0.25-750 is identical to the result of the adsorption of Auramine-O dye on ACs in the H 3-5 solution, and the dye adsorption quantity increases with the pH value [23]. Therefore, when the dye liquid pH > 5, the quantities of BY2 and BG4 dyes adsorbed by P200-0.25-750 become balanced, and there is no obvious change, which is identical to the result of Hameed and El-Khaiary (2008) [49], meaning that there is no significant change in adsorbance when the pH > 5 solution in the adsorption of malachite green dye on bamboo ACs. In addition, the adsorption of BY2 and BG4 dye liquids with different pH values on P200-0.25-750 is similar to the previous findings of adsorption of BY2 or BG4 dye liquid with different pH values on ACs [49], [74], [78].

G. Dye Desorption from ACs

The dye desorption test contributes to understanding the adsorption mechanism of ACs for dyes. DI water, HCl, and NaOH are often used as the eluents or desorption testing [23]. As the dye molecules adsorbed on the ACs can be desorbed by DI water, the dye molecules adhere to the ACs by the weak bonds, e.g. Van der Waals force [59], and can be desorbed by HCl or NaOH, meaning the dye adheres to ACs through ion exchange [31], [58]. This study used DI water, HCl, and NaOH to study the desorption rate (E_d) of BY2 dye on P200-0.25-750, which was 0.9, 0.3 and 1.4%, respectively, and the E_d of BG4 dye on P200-0.25-750 was 1.5, 0.5 and 1.7 % (not shown in Table). Therefore, the adsorption process of BY2 and BG4 dyes on P200-0.25-750 has simultaneous physical adsorption and ion exchange mechanisms [59]. Mall et al. (2006) [23] also uses DI water, HCl, and NaOH to desorb the Auramine-O dye on ACs, and the E_d is 3.7, 2.1 and 1.4%, respectively. This result was similar to the result of this study. However, the dye

desorption rate was relatively low in this study, as also stated by Mall *et al.* (2006) [23], meaning there are some complexes formation between the active sites of ACs and the functional groups of dye.

IV. CONCLUSION

This study used wood ash as the natural activating agent and different precarbonized specimens as the precursor, and prepared ACs by two-stage composite activations with wood ash and steam, in order to investigate the characterization of the prepared ACs, and their feasibility in dye adsorption. The yield and iodine value of the prepared ACs were 9.1-21.3% and 502.4-1171.1 mg/g. The S_{BET} of precarbonization and the wood ash-steam activation temperature of $750^{\circ}C$ in two-stage composite activations was 1619-1758 m^2/g and the V_{mi} was 0.26-0.33 cm^3/g, which was higher than that of K_2CO_3 activation, and the required activation temperature was lower than K_2CO_3 activation. The granular ACs with high yield 14.9%, S_{BET} 1619 m^2/g and S_{ex} 940 m^2/g was able to be prepared under the conditions of precarbonization temperature $200^{\circ}C$, ash to water ratio of 0.25 wt%, activation temperature of $750^{\circ}C$, steam flow of 0.5 mL/min, and activation duration of 1.0 h (P200-0.25-750). The nitrogen adsorption-desorption isotherms type were Type IV (micropore structure, mostly mesopores, and wide pore size distributions). The absorption of BY2 and BG4 dyes on P200-0.25-750 had simultaneous physical adsorption and ion exchange mechanisms, the maximum adsorbance was 625.0 mg/g and 769.2 mg/g, and the Langmuir isotherm analysis had better suitability than Freundlich. In the scope of this study, it is feasible to replace a chemical activating agent with natural wood ash in preparing ACs, and the ash content after the combustion of wood pellets can provide a reference for the preparation of ACs through activation, in order to implement environmental waste reduction and wood ash waste recycling, and thus, reduce the consumption of chemical activating agents, and their derived environmental pollution, to implement Cascade type and sustainable utilization of forest resources.

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Chia-Wen Peng was born in Nantou, Taiwan, and obtained his B.Sc. in forestry products science from National Chiayi University, M.Sc. in the Department of Forestry, National Chung Hsing University, and PhD degree at National Chiayi University, Taiwan. His PhD thesis is "Preparation of activated Carbon by activation with Japanese cedar wood ash and its dye adsorption capacity". This paper is portion of his PhD thesis. He has been working in the Experimental Forest, College of Bio-Resources and Agriculture, National Taiwan University, Nantou, Taiwan.

Han Chien Lin completed his PhD degree at Technology of Forest Products, Division of Bioenvironmental Sciences, he graduated school from Kyushu University in Japan, under the supervision of Professor Y. Murase, on Bio-functional materials. He was an assistant and associated professor at National Chiayi University, Taiwan from 2002 to 2009. He has been continuing as a professor at the same University. His research interests include wastes and pollution treatments of environmental resources, developments of forest products functional materials, and utilizations of forest products resources.