A clean process for activator recovery during activated carbon production from waste biomass

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ABSTRACT

Chemical activation is a widespread method for activated carbon (AC) preparation, but the removal and recycle of activator from the carbon product are generally a nuisance process. In this study, an environmental benign process, called modified vacuum pyrolysis (MVP) process, was developed for AC production and simultaneous recovery of the activator. The process included two steps: (1) carbonization and activation stage in a vacuum condition; (2) zinc recovery stage in a special temperature and pressure range. In the MVP process, over 99.99 % of the zinc used for activation was recovered in the form of zinc chloride and metallic zinc. The resultant ACs with basic and hydrophobic surface properties displayed higher adsorption capacity for phenol than that of carbons obtained by traditional pyrolysis method. The main merit of the MVP process was that there was no wastewater generation during the whole procedure. Consequently, the experimental data obtained in the present study provided scientific basis for zinc chloride recovery by vacuum pyrolysis during ACs production process.

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1. Introduction

The total amount of biomass resources is equivalent to 650 million TCE (ton of standard coal equivalent) per year in China [1]. This type of resource includes residues from agriculture and forestry, and the organic component of municipal and industrial wastes. Due to the absorption of carbon dioxide in its production process and less sulfur and ash content than coal, biomass is not only a clean but also a low-carbon fuel which becomes a sink for the greenhouse gases [2]. Currently, biomass energy is reviewed as one of the most promising renewable energy resources.

In the last decades, waste biomass energy was mainly consumed in rural areas of China by direct combustion. However, with social and economic development, a lot of rural people have been transferring into urban area gradually, and as a result the direct combustion of biomass has been decreasing in the recent years. Therefore, great interests have been paid for biomass to realize the value-added utilization by modern processing technologies, such as pyrolysis, gasification, and liquefaction [3]. However, the industrialization of bio-fuels production still confronts several challenges: (1) lower the cost of the bio-energy; (2) reduce the adverse environmental effect during the process of production and utilization of bio-fuels; (3) and produce a variety of energy and material products from biomass.

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Activated carbons (ACs) are known as versatile materials which have been studied as adsorbents, catalysts and catalyst supports for different purposes. However, wildly using these materials tends to be expensive due to their high production costs. Many studies exploited waste biomass as precursors for ACs to reduce the production cost [4–6]. However, little attention has been paid for both simplifying and reducing the cost of the ACs production technology. The most commonly used methods for the preparation of ACs are based on so-called physical or chemical activation. A comparison of chemical activation against physical activation shows that chemical activation provides higher yield, lower temperature of activation (less energy costs), less activation time and, generally, higher development of porosity. The disadvantages of the chemical activation are the consumption of relatively expensive activating agents and the problems related to the washing and re-utilization of these agents [7]. As one of the commonly used activating agents, zinc chloride remains almost unchanged after chemical activation, thus it can be recycled by the traditional acid washing process. However, this recovery process is not only time consuming but also produces a large amount of wastewater, resulting in secondary pollution. Previous studies demonstrated that vacuum pyrolysis was an effective separation method in metallurgy for materials with different vapor pressure [8–10]. Furthermore, no off-gas and wastewater were produced during vacuum pyrolysis process thus this is an environmentally benign process. As for biomass conversion, vacuum pyrolysis was primarily used for bio-oil production [11–13]. In the recent years, researchers started to use vacuum

pyrolysis for pretreatment or activation in ACs production, and significant improvements of ACs performance were achieved [14–20]. To the best of our knowledge, there is no report related to the activating agents recycling from ACs by vacuum pyrolysis. In this study, vacuum pyrolysis was applied for chemical recovery from ACs.

The objectives of this research were to: (1) examine the possibility of converting typical waste biomass in China into high quality ACs; (2) develop an environmental benign process for the ACs production achieving the recovery of chemical activator simultaneously; (3) optimize various parameters for the process and characterize the properties of the obtained AC.

2. Experimental details

2.1. Materials

Sawdust (pinewood) was used as the representative material. The raw material was obtained from a wood processing factory in Beijing suburb. Prior to use, the raw sawdust was oven dried for 48 h at 105 °C, then crushed and sieved to <80 meshes. The proximate and ultimate analyses of this material are shown in Table 1. This waste may be considered as a good candidate for conversion to AC because of its relatively high carbon content and low ash. Chemical pure zinc chloride was purchased from Beijing Chemicals Company and used without any further purification.

2.2. ACs preparation and activator recovery

Activation was performed as follows: a certain amount of dried raw material was mixed with zinc chloride solution with impregnation ratio 1:1 (mass basis) for about 6 h at 80 °C, and then the resulting homogeneous slurry was dried at 110 °C overnight. The activation of the impregnated material was conducted in a tubular furnace connected to cold traps. The cold traps were ice cooled for collecting volatiles and followed by a mechanical vacuum pump (ULVSC, GLD-051). The vacuum pump fitted with flow control devices could be adjusted from 0.1 to 100 kPa. In each run, the system was vacuumed to a certain pressure, and then heated to a desired temperature (400–800 °C) for a certain time at a fixed ramping rate. The reactor systems were cooled to room temperature under vacuum condition. The carbon and chemical samples collected from reactors and cold traps were weighed and kept for further treatments, respectively.

2.3. Characterization of the ACs

Zinc residues in samples before and after carbonization were analyzed by an inductively coupled plasma-optical emission spectrometry (ICP-OES, PerkinElmer, USA) after digesting with nitric acid, hydrofluoric acid and perchloric acid. There was 26.50 wt.% of zinc initially impregnated in the sawdust, and the amount of zinc recovered from ACs was calculated by:

$$\text{Recovery rate of Zn (\%)} = \frac{(\text{mass of Zn impregnated} - \text{mass of Zn in the ACs})}{(\text{mass of Zn impregnated})}$$

Table 1
Proximate and ultimate analysis of the raw material.

Proximate (wt.%, dry basis)		Ultimate (wt.%, dry and ash-free basis)	
Moisture	4.02	Carbon	47.57
Volatile matter	76.64	Nitrogen	0.45
Fixed carbon	18.89	Hydrogen	6.57
Ash	0.45	Oxygen (by difference)	45.41

Thermogravimetric analyses (TGA-2050, TA Instruments, USA) were carried out to investigate the thermal behavior of zinc chloride. About 40 mg of chemical pure zinc chloride was heated from 30 to 900 °C at a ramping rate of 10 °C min^{−1} under flowing nitrogen. The pore structure characteristic of the activated carbon was determined using nitrogen as an adsorbate at 77 K in an automatic apparatus ASAP 2000 Micromeritics (USA). The BET surface area was calculated from the isotherm using the Brunauer–Emmett–Teller (BET) equation. The crystalline structures of the ACs and condensates were examined by X-ray diffractometer (Philips PW, model 1700, Netherlands) using Cu K α radiation at 40 kV and 40 mA and scanning at a speed of 3° min^{−1}.

The surface chemistry was analyzed by FT-IR spectroscopy, pH of the point of zero change (pH_{PZC}) and SEM-EDX analysis. FT-IR spectra were determined in the range of 600–4000 cm^{−1} using potassium bromide pelletization method on a Nicolet Nexus 670 spectrophotometer (USA). The pH_{PZC} of the carbon samples were measured using the pH drift method [21]. The pH of a solution of 0.01 M sodium chloride was adjusted between pH 2 and pH 12 by adding either hydrochloride or sodium hydrate solution. A total of 0.10 g of activated carbon was added to 25 mL of the solution. After the pH had stabilized (typically after 24 h), the final pH was recorded. The graphs of final pH versus initial pH were used to determine the points where the initial pH was equal to the final pH. This point was taken as the pH_{PZC} of the carbon. The surface morphology and elements were studied by scanning electron microscope – energy dispersive X-ray spectra (SEM-EDX, HITACHI S-3000 N, Japan).

2.4. Adsorption experiment

The adsorption of phenol from aqueous solution on the activated carbons was carried out at 25 °C by using 0.10 g of carbons added into 100 mL of phenol solution with initial concentration of 100 mg L^{−1} in stoppered flasks. They were kept in a thermostat shaker bath at 25 °C for 2 days, after which the equilibrium concentration was determined spectrophotometrically (UV-2450, Shimadzu, Japan) at the maximum absorbance wavelength of 269 nm [22].

3. Results and discussion

3.1. Zinc recovery rate

The effects of pressure and temperature on zinc recovery rate during the pyrolysis process are shown in Fig. 1. As can be seen, the zinc recovery rate dramatically increased with the temperature

Fig. 1. Effects of pressure and temperature on zinc recovery rate (holding time = 30 min, heating rate = 20 °C min^{−1}).

rising from 400 to 600 °C. At the same time, lower system pressure below 50 kPa could also effectively favor zinc recovery during this temperature range, e.g., the amount of zinc recovered at 500 °C is increased from about 40 % at 100 kPa to 90 % at 1 kPa. According to the thermal behavior of pure zinc chloride under atmosphere pressure (Fig. 2), it can be seen that the evaporation of zinc chloride started at 400 °C, and almost all of them could evaporate into gaseous phase when the temperature is above 700 °C (about 0.02 % ash remained). However, after impregnated with carbonaceous material, about 10 % of zinc still remained in the carbonized materials at the temperature up to 700 °C, and reducing system pressure had little effect on the zinc recovery rate during 600–700 °C. The results showed that around 99.99 % of zinc was recovered within 30 min by reducing system pressure below 20 kPa at 800 °C.

Comparing Fig. 1 with Fig. 2, it can be seen that the complete extraction of activator after impregnation with carbonaceous materials requires higher temperature than that of pure zinc chloride. There might be several reasons hindering the activator recovery from AC products. On the one hand, the carbon materials after activation have abundant porous structures and functional groups, thus the physical and chemical adsorption between carbon and residual activator might inhibit effectively removing of activator in low temperatures. On the other hand, chemical reactions might happen to zinc chloride during the activation process and generate other substances. The carbonized samples obtained at various temperatures and pressures were analyzed by XRD analysis (Fig. 3). The formation of crystal zinc oxide was detected with the activation temperature above 400 °C (Fig. 3a). The higher boiling point (2360 °C) and decomposition temperature (1975 °C) of zinc oxide is one of the reasons for hindering complete recovery of zinc from carbon products below 800 °C. Meanwhile, the amount of zinc chloride detected in the carbon products at 700 °C indicates that there are strong adsorption effects between the carbon material and the activator (Fig. 3a). Rising temperature from 400 to 600 °C at 50 kPa (Fig. 3a) or lower pressure from 100 to 20 kPa at 500 °C (Fig. 3b) both increased the intensities of diffraction peaks of zinc oxide, which is due to the enhancement of crystallization. With the disappearance of zinc oxide peaks from the AC obtained at 800 °C, 20 kPa, metallic zinc could be detected in the condensate, otherwise, zinc chloride and its hydrates could be mainly collected during 400–600 °C in the condensers (Fig. 3c). It can be deduced that the amount of zinc recovered below 600 °C mainly caused by the evaporation of zinc chloride. Lowering pressure from 100 to 20 kPa could reduce the boiling point of zinc chloride from 532 to 432 °C, thus lowering pressure enhanced the zinc recovery greatly below 600 °C. When it comes to higher temperatures, zinc oxide became the major chemical residue in the ACs. Then the zinc

recovery process involves the redox reaction between zinc oxide and carbon and the evaporation of the metallic zinc, which is much more complex and needs more stringent conditions. Detailed discussion is in the following text. Due to the profound discrepancy of condensing temperature between metallic zinc and zinc chloride, they will be condensed at different temperature regions of the collector, thus effective separation of them could be achieved. During the pyrolysis process, the following chemical reactions might occur: firstly, zinc chloride hydrolyzed during the impregnation process. Thermal treatment decomposed the hydrates of zinc chloride, causing the formation of volatile hydrochloric acid [23]. Meanwhile, an acid–base cement like material ($\text{Zn}_2\text{OCl}_2 \cdot 2\text{H}_2\text{O}$) was found in the ACs at 400–500 °C (Fig. 3). The cement like material was mainly in amorphous phase with a little crystalline phase [24,25]. When the temperature was above 400 °C, the compounds decomposed into volatile zinc chloride, steam, and solid zinc oxide (Eq. (2)). Raising temperature from 400 to 600 °C or lowering pressure from 100 to 20 kPa both promoted the evaporation of zinc chloride, thus enhanced the formation and crystallization of zinc oxide. Finally, the residual zinc oxide was removed by carbothermal process [26,27] shown in the following equation:

According to previous reports, carbothermal reduction of zinc oxide and effective recovery of zinc could be achieved at about 1200–1300 °C [28], and moreover, Mariusz Grabda, etc. proposed that the reaction temperature could decline to around 1000 °C by mixture of waste polyvinyl chloride or tetrabromobisphenol A with the reactors [29,30]. In this study, when system pressure was below 20 kPa, almost total zinc recovery could be achieved at 800 °C, thus lowering system pressure had not only declined the carbothermal reaction temperature but also enhanced the metal evaporation velocity [10]. Thermodynamic analysis of the carbothermal reaction further demonstrates this point (shown in the following equation):

$$\Delta G = \Delta G^\theta + RT \ln \left[\frac{P_{\text{Zn}}}{P^\theta} \right] \left[\frac{P_{\text{CO}}}{P^\theta} \right] \quad (4)$$

where ΔG is the Gibbs free energy at a certain temperature (J), R the universal gas constant, T treatment temperature (K) and P system pressure (Pa), P^θ the saturated pressure of metallic zinc at a certain temperature (Pa).

The redox reaction could take place when $\Delta G < 0$. The reaction temperature could be reduced from 948 °C at 100 kPa to 800 °C when the system pressure decreased to 20 kPa, and at the same time the evaporation velocity of metallic zinc increases sharply with the pressure lower than the saturated vapor pressure at 800 °C (about 30 kPa). However, with further decreasing of the pressure to 0.2 kPa ($\Delta G = 0$ J, $T = 522$ °C), few metallic zinc was obtained in the condenser within 30 min at 522 °C, indicating that the reduced zinc could not be effectively recovered. Therefore, the key factor restricting zinc recovery rate below 800 °C was the evaporating velocity of the reduced zinc. This could be attributed to the fact that the saturated vapor pressure of metallic zinc is significantly reduced at lower temperature, e.g., at 800 °C, the saturated vapor pressure of metallic zinc is about 30 kPa, while at 500 °C the saturated vapor pressure is merely 0.018 kPa. Moreover, the activated carbon with large surface area also inhibited zinc evaporation at low temperature.

From the theoretical and experimental results stated above, it could be concluded that there are two steps included in the chemicals recovery process, namely zinc chloride evaporation process

Fig. 2. Thermogravimetric analyses (TGA) in a nitrogen atmosphere of zinc chloride (heating rate = 10 °C min⁻¹).

Fig. 3. XRD patterns of condensates (c) and ACs obtained at different temperatures (a) and pressures (b) (holding time = 30 min, heating rate = 20 °C min⁻¹).

below 600 °C and carbothermal reduction of zinc oxide above 800 °C, only when the pressure was less than 20 kPa the zinc oxide could be effectively removed within 30 min at 800 °C. Compared with other pyrometallurgical methods for zinc recovery from zinc oxide, vacuum pyrolysis not only consumed less energy but also obtained higher removal efficiency.

3.2. Characterization of the obtained carbons

The effects of temperature and pressure on the bulk properties and the yields of the obtained products are presented in Fig. 4. In the pressure range studied in this paper (1–100 kPa, at 500 °C), the maximum surface area, total pore volume and yield of carbon are observed at 50 kPa, and the minimum of the average pore diameter also occurred at this point. It was demonstrated that

decreasing system pressure in a certain range can reduce the oxygen in the system and the residence time of organic vapor. Low residence time of organic vapor limits the secondary reactions which form carbonaceous deposits on the surface and in the pores of the ACs [15]. The surface area and total pore volume decline sharply with pressure decreasing from 50 to 20 kPa, then hold steady when the pressure less than 20 kPa (Fig. 4a). However, a continuous yield decrease and pore size increase can be observed with pressure decreasing from 50 to 1 kPa (Fig. 4b), which is attributed to the vigorous volatilization of pyrolysis vapor. In the temperature range studied in this paper (400–800 °C, at 50 kPa), the surface area, pore volume and yield continuously decrease while the average pore size fluctuates with temperature increasing. The dramatic shrinkage of the porosity was coincident with the violent evaporation of zinc chloride with the effects of pressure and temperature

Fig. 4. Effects of pressure and temperature on surface properties and carbon yields of the activated carbons (holding time = 30 min, heating rate = $20^{\circ}\text{C min}^{-1}$). S_{BET} = BET surface area, V = total pore volume, Yields = carbon yields, D = average pore diameter.

shown in Fig. 2. In a previous report, it was claimed that zinc chloride worked as dehydration reagent and restricted the formation of tar and promoted the charring of the carbon below the carbonization temperature of the precursor [31]. Thus, excessive evaporation of zinc chloride prior to the carbonization could decrease the activation effect resulting in the decrease of specific surface area and total pore volume. Also, the vigorous volatilization of pyrolysis vapor would destroy the microporous structure and lower the yields of AC shown in Fig. 4b. It can be concluded from Fig. 4 that the maximum of specific surface area, total pore volume and carbon yield of the AC were obtained at 50 kPa and 400°C , which is optimum for AC production.

Combining the effects of temperature and system pressure on zinc recovery and AC quality (Fig. 1 and Fig. 4), it can be concluded that the suitable temperature and pressure for the AC production is 400°C and 50 kPa, where microporous carbon with high specific surface area, total pore volume and carbon yield can be obtained. However, the effective domain for the zinc recovery is 800°C and <20 kPa, which is applicable for zinc oxide reduction and zinc removal in an appropriate time span. It can be seen from Fig. 4 that decreasing the system pressure from 20 to 1 kPa had little effects on the porosity of ACs, but significant heat shrinkage of the porosity could be observed by increasing the temperature from 400 to 800°C , thus applying 1 kPa at 800°C could effectively increase the evaporation rate of the chemicals, and then decrease the holding time of ACs at high temperature. It can be observed by the white smoke in the condensers that the removal and evaporation of residual zinc only lasts for a few minutes. In order to completely

remove zinc chloride and simultaneously obtain highly quality AC, the vacuum pyrolysis was modified. Firstly, a medium system pressure (50 kPa) was applied at temperature rising period ranging from 30 to 400°C and kept at 400°C for 1 h. During this stage the carbon structure was modified and the porosity increased. Secondly, low system pressure (1 kPa) was applied at temperature rising period from 400 to 800°C and kept for 10 min. The results indicated that the zinc content of the AC obtained by modified vacuum pyrolysis (MVP) was less than 0.01 wt.%, meeting the standard for ACs application on drinking water treatment [32]. Furthermore, the AC obtained by MVP process had higher specific surface area, total pore volume and AC yield ($1350 \text{ m}^2 \text{g}^{-1}$, $0.64 \text{ cm}^3 \text{g}^{-1}$ and 42.54 wt.% respectively) than those of ACs obtained by traditional vacuum pyrolysis at 800°C . Therefore, MVP is an effective way to recycle chemicals and obtain highly porous ACs.

Fig. 5 compares the FTIR spectra of the ACs prepared by MVP process and traditional process (500°C , nitrogen atmosphere). The washed and unwashed ACs obtained by traditional process are denoted as 500-AW and 500-UW, respectively. As can be seen from Fig. 1, about 60 wt.% of zinc remained in the 500-UW. Thus significant differences can be observed from FTIR spectra between 500-UW and 500-AW. The strong absorbance peaks appeared at 1615 and 3571 cm^{-1} in 500-UW are mainly due to the chemicals remained in the carbonized material. After removing chemical activating agents by acid washing the functional groups that are often observed in ACs in FTIR analysis, namely alkenes, esters, aromatic, ketones, alcohol, hydroxyl and carboxyl, are found on the surface of 500-AW. With the help of the literatures, the bands at $3200\text{--}3600 \text{ cm}^{-1}$ and $950\text{--}1300 \text{ cm}^{-1}$ are assigned to the O–H and the C–O stretching vibration mode of hydroxyl functional groups including H bonding and indicating the presence of phenol, esters, ethers groups. The bands at $2800\text{--}3000 \text{ cm}^{-1}$ indicate the presence of aliphatic C–H stretching, and at 1687 cm^{-1} indicates stretching of conjugated C=C or aromatic-oxygen bond in aromatic ether. The bands around 1434 cm^{-1} are assigned to C–H or --CH_2 groups, which are overlapped [33]. Those groups detected from the ACs surface are mainly oxygen-containing acidic groups.

On the other hand, for the ACs obtained by MVP process, due to the complete removal of activators, there are little differences between the FTIR spectra before or after acid washing, e.g., only a little increase of intensity of 3255 cm^{-1} is observed after acid washing process, attributing to the hydrogen-bonded groups. However, the FT-IR spectrum of AC obtained from MVP process is quite different from that of carbon obtained from traditional pyrolysis. A remarkable decrease in the intensity of 3380 cm^{-1} , and the disappearance of bands at 1014, 1287, 1687 cm^{-1} indicate that the MVP treatment decomposes the oxygen functional groups in the carbons, and this could be attributed to the decomposition of the carboxylic acid groups and partial intermolecular rearrangements to form lactone groups. The appearance of absorbance peaks on the range of $1700\text{--}1780 \text{ cm}^{-1}$ indicating the presence of ketones and aldehydes also confirm the inference. The band around 1516 cm^{-1} , 734 cm^{-1} , 861 cm^{-1} attributed to aromatic stretching are clearly observed, suggesting the AC becomes increasing polyaromatic after MVP treatment. The surface functional groups play an important role in many properties of ACs, in particular their wetting and adsorption behavior. Chemical activation always results in oxygen-containing polar groups being covalently bound to the carbon surface besides the development of porous structure in the material. Most of the surface oxides are acidic, and they provide hydrophilic sites. Therefore, the adsorption capacity for polar and basic materials can be significantly improved. While treating ACs under MVP process has selectively removed some of these functional groups. Carbons with a low oxygen content exhibit basic surface properties and an anion

Fig. 5. FT-IR spectra of acid washed and unwashed ACs. 500, MVP = ACs obtained at 500 °C, atmosphere pressure; or under modified vacuum pyrolysis. AW, UW = acid washed or unwashed.

Table 2

Comparisons of the ACs obtained by MVP process and traditional process.

Sample	Wastewater (L g ⁻¹)	Zn (wt.%)	Cl (wt.%)	Ash (wt.%)	V _T (cm ³ g ⁻¹)	V _{Mic} (cm ³ g ⁻¹)	S (m ² g ⁻¹)	pH _{PZl}	Phenol ^d (mg g ⁻¹)
500-AW ^a	2	<0.01	2.35	0.21	0.79	0.62	1675	5.37	166
MVP-AW ^b	1	<0.01	1.82	0.39	0.66	0.59	1359	7.01	214
MVP-UW ^c	–	<0.01	0.08	3.85	0.64	0.58	1350	7.25	237

^a Activated carbon obtained at 500 °C under atmosphere pressure after acid washing.

^b Activated carbon obtained by modified vacuum pyrolysis after acid washing.

^c Activated carbon obtained by modified vacuum pyrolysis before acid washing.

^d Phenol adsorption capacity obtained at 25 °C.

exchange behavior, which could enhance the adsorption capacity of acidic contaminants [36].

The higher value of pH_{PZl} of MVP-UW (shown in Table 2) also indicates that the basicity and/or hydrophobic surface properties of the carbon can be obtained by removing the acidic oxygen-containing surface groups by the MVP process. From Table 2, it can be seen that removing of residual zinc from a gram of AC by traditional acid washing process will produce about 2 L of wastewater containing various metal elements. Thus the treatment of the wastewater was difficult and costly. Alternatively, the MVP process can effectively remove zinc from ACs, and at the same time the activator recycled could be used directly, moreover, no wastewater was produced.

3.3. Phenol adsorption

The phenol adsorption capacities of ACs obtained by MVP process and traditional pyrolysis are displayed in Table 2. It can be seen that ACs obtained from MVP process display superior adsorption capacity for phenol than that of 500-AW. At the same time, demineralization of the carbons by acid washing also had a negative effect on phenol adsorption. It has been reported that the most important characteristics of AC in the adsorption of organic compounds were pore size distribution, surface chemistry, and mineral matter content [34]. Phenol is a small (10 Å) and weakly acidic molecule, which tends to be adsorbed on the microporous and basic ACs [35,37]. However, the highest phenol adsorption (237 mg g⁻¹) was obtained by MVP-UW which has lowest micropore volume but highest pH_{PZl} value among the other ACs

compared (Table 2). Thus it can be concluded that the basicity surface chemistry played a decisive role in the phenol adsorption process in this study, which was consistent with previous reports [22]. It has been reported that the basic and hydrophobic ACs are more stable at ambient conditions [36], and have predominant adsorption capacity for non-polar and acidic materials [37]. The MVP increased the phenol adsorption capacity by removing the acidic oxygen-containing surface groups, while the acid washing process showed the opposite effect. It has been found that the demineralization treatments with hydrochloride lead to small amount of chloride adsorbed on the surface of the carbons, which was detected by EDX and shown in Table 2. The adsorbed chloride would decrease the surface basicity of the carbons by localizing the electrons, thus inhibiting the formation of electron donor–acceptor complexes with phenol [22]. Therefore, MVP process could not only recycle the chemicals without any wastewater generation, but also modified the surface chemistry for phenol adsorption.

4. Conclusions

This study developed an environmentally benign process, called modified vacuum pyrolysis (MVP) process, for AC preparation from waste biomass with the activating agent recycling simultaneously. Using MVP, 99.99 % of zinc was recovered from ACs during the production process without any wastewater production. The temperature and pressure were two key parameters affecting the recovery rate of the chemicals and the porosities of the resultant AC. The resultant AC has superior physical properties with BET surface area 1350 m² g⁻¹ and pore volume 0.645 cm³ g⁻¹, respectively. Further-

more, the surface chemistry of the AC tended to be basic and hydrophobic, and this resulted in a higher adsorption capacity for phenol than that of AC obtained by the traditional pyrolysis process. Therefore, the MVP process is a potential alternative for zinc chloride chemical activators removing and recycling during AC production from waste biomass.

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