A Comparative Study on Adsorbing Gaseous Formaldehyde with Novel Biomass Activated Carbons from Agriculture Wastes at Ambient Temperature

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Abstract. To remove gaseous formaldehyde (HCHO) and rationally utilize agriculture wastes, chemical activation method using ZnCl₂ as activating agent was employed to develop high-class biomass activated carbons (BACs) derived from agricultural straws for HCHO removal at ambient temperature. Proximate analysis and ultimate analysis testified that these agricultural straws were appropriate BACs precursors. BACs’ physicochemical properties were characterized by BET, SEM, FTIR and TGA, which demonstrated BACs with large specific surface area had the potential as ideal adsorbents. Systemic tests investigated the effects of activating agent (ZnCl₂) and the concentrations of O₂ and HCHO on adsorption performances of BACs, and compared them with two commercial activated carbons (CACs). Results showed ZnCl₂ brought enormously positive effects but O₂ had a prohibitive effect on the adsorption performance. BACs exhibited better performance than CACs, and BACM (BAC derived from maize straw) could obtain more than 80% removal efficiency under 1ppm HCHO after 40h. Desorption and regeneration tests were conducted to evaluate the security of the adsorbent and recycle regenerated adsorbent. The desorption temperature all above 50℃ could ensure use security indoors. Saturated BACM through 1 or 2 run regeneration still exhibited better adsorption performance compared with virgin CAC from coal, indicating that the regeneration was significantly meaningful in practical application.

1. Introduction

Formaldehyde (HCHO) commonly emitted from decoration and building materials has prompted a critical increasing concern throughout the world due to its severe harms on human health even at extremely low concentration[1-2]. Even upon single exposure to HCHO, it can invade the mucous membrane of the exposed human body such as eyes and nose. Besides, long term exposure, people
may develop weakness, diarrhea, coughing, skin disease (atopy), emotional instability, lethargy, headache and amnesia[3]. What is worse, HCHO is also identified as a potential human carcinogen and leukemogen, eventually leading to death[4-5]. Therefore, the removal of HCHO is excessively urgent and meaningful allowing for eliminating the adverse effects from HCHO and satisfying the stringent environmental regulations. Unremitting efforts have contributed to many physico-chemical processes for HCHO removal, such as adsorption and catalytic oxidation or photocatalytic oxidation[6]. Catalytic oxidation and photocatalytic oxidation are recognized as the hopeful technology for HCHO removal, nevertheless, the former often exhibits good performance at high temperature (>50℃) and may be very likely over noble metal catalysts[7-8], and photocatalytic decomposition demands illumination by light sources[9-10]. Based on energy-saving and environmental-friendly reaction product consideration, the development of appropriate catalysts with the ability of complete oxidation of HCHO at ambient temperature under very low concentrations is consumingly desirable, but it is still an enormous challenge to be solved. Studies showed that HCHO could be photocatalytically decomposed at high concentration, but once the concentration dropped below 1 ppm, the photocatalytic decomposition promptly slowed down and subsequently almost terminated, which limited its application in indoor air purification because the concentration of indoor HCHO was often below 1 ppm[11]. Moreover, to some degree, catalytic or photocatalytic oxidation is not convenient and even not feasible for indoor HCHO removal without thermal and photon sources. Therefore, although adsorbents suffer from some inherent shortcomings such as limited removal capacities, adsorption is a practicable and reliable approach to decrease HCHO in some situations. Thereinto, adsorption by activated carbon (AC) was widely used as the highly effective HCHO removal method because of the low operating costs, low energy consumption and the flexibility of the removal system[12-13]. However, despite the relatively low operating costs of ACs, adsorption still needs to cost money since commercial ACs are currently derived from relatively expensive and nonrenewable raw materials such as bituminous coal and wood.

At the same time, China as a big agricultural country produces hundreds of millions of tons of agriculture straws every year and our country is experiencing the challenge from the dispose of these renewable agriculture wastes since most of them can not receive reasonable utilization and be open burning (OB)[14], which can seriously aggravate air quality causing adverse human health effect and deteriorate road traffic and flight safety, receiving growing concern. Notably, the Asian developing countries have been undergoing frequent haze problems in recent several decades, biomass open burning (OB) smoke was reported to be a cause of the repeated occurrence of transboundary haze event, especially during the harvest season[15-17]. Wherein, crop residue OB contributed more than 80% of the total biomass OB emissions[16]. Therefore, the reasonably beneficial utilization of agricultural straws is urgently imperative and the unit of environmental and economic benefits can be reached. As a result, it is enormously monetary and environmentally friendly incentive for manufacturing affordable activated carbon derived from these agriculture wastes. Furthermore, the combination of the win-win approach to agriculture wastes and cost saving of HCHO removal which offsets the limited adsorbent capacities of adsorbents is of significantly practical interest.

Fortunately, agricultural straws, the inevitably agricultural by-products, have also been researched for reuse and beneficial disposal in recent years, for example, they can be used for manufacturing BACs[18-19]. However, these BACs have main applications on waste water treatment[20-21]. Besides, they are also used for gas purification such as NO treatment[22] and mercury removal[23], nevertheless rarely even never used for HCHO removal. In addition, as we know, ideal adsorbents should possess preeminent interlinked pore property, excellently big surface area, and abundant superficial functional groups. Therefore the AC prepared by traditional methods without activation owned very small BET[24], and it was reported that the AC prepared with chemical activation adopting ZnCl2[21], H3PO4[22] and KOH[18] could obtain a larger BET and improve the property of the adsorbent materials. In this work, the BACs with ZnCl2 activation derived from the most common agricultural straws (rice straw, wheat straw and maize straw) were prepared and the preparation condition was explored and optimized aiming at finding affordable and high-performance activated carbons from agriculture straws for HCHO removal. We investigated the effects of activating agent and the concentrations of
O₂ and HCHO on the adsorption performances, analyzed and compared the adsorption performances of the BACs with two commercial activated carbons (CACs) derived from coal (CACC) and wood (CACW). The surface areas and porous structures as well as surface properties of the activated carbons were characterized by BET, SEM, FTIR and TGA. Besides, the desorption and regeneration tests were also conducted to estimate the security of the adsorbent and the recycled adsorbent.

2. Experimental

2.1. Preparation of samples
The rice straw, wheat straw and maize straw are collected from the rural areas of Xinyang city, Henan province, PR China. These raw materials were first rinsed with deionized water and dried at 105°C overnight, crushed and sieved for standby application. The resulted particles (RPs) were impregnated into calculated ZnCl₂ solution (the mass ratios of activating agent (ZnCl₂) and RPs were 0.5, 1, 1.5 and 2) for 24h at ambient temperature. In order to compare the possible influence of ZnCl₂, meanwhile some RPs were impregnated into the deionized water. After that, the treated materials were dried at 105°C overnight, and subsequently they were activated in a tube-type electronic heating furnace at certain activation temperature (450°C, 550°C, 650°C, 750°C and 850°C) for certain activation time (0h, 0.5h, 1h, 2h and 3h) under purified N₂ solution and therewith rinsed with deionized water. At last, the obtained BACs were dried at 90°C in the oven to a constant weight for use. The RPs from rice straw, wheat straw and maize straw were named RPr, RPw, and RPM, respectively. The BACs derived from rice straw, wheat straw and maize straw underwent ZnCl₂ activation or without ZnCl₂ activation were called BACR or BACR0, BACW or BACW0 and BACM or BACM0, respectively.

2.2. Characterization of samples
The proximate analysis in terms of moisture, volatile matter, fixed carbon and ash contents was conducted according to ASTM D3173-3175 standards. The elemental analysis was carried out by the Elementar Analysensysteme GmbH vario (Elementar Ltd, Corp, Germany). Surface areas and porous structure property of the samples were characterized by an automatic Micromeritics ASAP2460 volumetric sorption analyzer (Micromeritics Instrument Corp., USA). Surface physical morphology was observed by Quanta 200 FEG MKII scanning electron microscope with a tungsten electron source, with 3nm resolution (Fei, USA). Fourier transform infrared spectroscopy (FTIR) was performed on a Infinity-1 (Shimadzu, Japan) spectrometer with a spectral resolution of 4cm⁻¹ and the spectrometer in a frequency range 4000 and 400 cm⁻¹ to qualitatively identify the functional groups. Prior to each measurement of FTIR studies, powders of the samples were grinded and mixed with KBr (200 mg, spectroscopically pure) before tableting on a hydraulic press. Besides, the thermogravimetric analyzer STA409PC/4/H(Netzsch Ltd. Corp., Germany) was employed to investigate the desorption of HCHO from the saturation adsorption activated carbon.

2.3. Experimental setup and procedure
The adsorption tests were conducted in a laboratory-scale fixed-bed system, which was shown in Fig.1. In each test, 300mg sample was loaded in a quartz reactor with an internal diameter of 10mm, generally the simulated flue gas (SFG) feed consisted of 30ppm HCHO about 36.2mg/m³, 6%O₂ and N₂ as balanced gas and the carrier gas of gaseous HCHO. The O₂ and N₂ gases were accurately controlled by mass flow controllers (MFCs). Gaseous HCHO was generated by a peristaltic pump which transferred condensed formaldehyde solution into teflon tube wrapped with temperature-controlled heating band (120°C). A flow of 150 mL/min pure N₂ used as the carrier gas of gaseous HCHO went through a condensing unite in an ice-water bath for removing water vapor mixed with the O₂ and balanced N₂ in the gas mixing chamber. The finally mixed gas again passed through a condensing unite in an ice-water bath to thoroughly eliminate water vapor. The inlet gas was monitored after the variation of HCHO concentration less than 5%. The total flow rate is 500 mL/min,
corresponding to a gas hourly space velocity (GHSV) of approximately 1.5×10⁵ h⁻¹. The regeneration tests were also carried out in the laboratory-scale fixed-bed system where the saturation adsorption activated carbon in the quartz reactor in a tube-type electronic heating furnace with a heating rate of 6°C/min and kept at 250°C under continuous N₂ gas until no HCHO could be detected outlet of the reactor.

HCHO concentrations at both the inlet and outlet of the reactor were monitored by a PGM-7340 (RAE, USA; detection limit = 1ppb). Blank tests in preliminary experiments demonstrated the influences from the reactor, and the gas pipes on HCHO removal were verified to be negligible. HCHO removal efficiency (E) of each sample was calculated by the following equation (1). HCHO adsorptive capacity Qt(mg/g) was determined according to equation (2).

\[
E = \left(1 - \frac{[HCHO]_{\text{out}}}{[HCHO]_{\text{in}}}\right) \times 100\% 
\]

\[
Qt = \frac{T \times [HCHO]_{\text{in}} \times Edt}{M} 
\]

Where, [HCHO]_{in} and [HCHO]_{out} respectively represented the inlet and outlet HCHO concentration (mg/Nm³) of the reactor. T was the total gas flow rate(Nm³/min), M was the mass of sorbent (g) and t was the adsorption time. Besides, to lessen the experimental error, the E and Qt was the average of two or three parallel experimental data and the relative error was less than 5%.

3. Results and discussion

3.1. Characterization of samples

3.1.1. Proximate analysis and ultimate analysis. The obtained BACs prepared by the method mentioned above were black, granular and inodorous, while the final yields of BACR, BACW and BACM from relevant BPs were 37.22%, 30.96% and 33.63%, respectively. The results of proximate analysis and ultimate analysis of BACs and CACs were enumerated in Table 1. Besides, the original RPs were also listed in Table 1 for comparison. As can be seen from Table 1, the high volatile matters of RPs as BAC precursors could be ejected under high temperature condition to form the rudimentary pore structure, which could be further activated to produce more luxuriant pore structure resulting in elevated adsorption capacity. Therefore, these RPs with high volatile matters could be deemed to be appropriate BACs precursors because the volatile matter could be an important requirement for justifying the suitability as AC precursors[12]. Notwithstanding these RPs had relatively low fixed carbon contents, after ZnCl₂ activation, the fixed carbon contents of BACs increased remarkably.
might be attributed to the activating agent of ZnCl$_2$ which could influence the pyrolytic decomposition and worked effectively as dehydration reagent\textsuperscript{[26]}, thus increasing the carbon yield. The contents of N, H, and S were meager while the contents of C and O were abundant, therefore the various element contents might contribute to forming different functional groups in these BACs, which might make a difference in their adsorption performance.

### Table 1. Results of proximate analysis and ultimate analysis.

| Sample | Moisture(%) | Volatiles(%) | Fixed carbona(%) | Ash(%) | C(%) | N(%) | H(%) | Oa(%) | S(%) |
|--------|-------------|--------------|------------------|--------|------|------|------|-------|------|
| RPm    | 1.6         | 73.8         | 17.9             | 6.7    | 40.32| 0.94 | 5.31 | 53.34 | 0.09 |
| RPw    | 0.9         | 74.4         | 17.4             | 7.3    | 39.13| 0.85 | 5.36 | 54.55 | 0.11 |
| RPr    | 1.4         | 72.7         | 18.3             | 7.6    | 39.18| 0.74 | 5.12 | 54.9  | 0.06 |
| BACM   | 1.9         | 21.1         | 68.7             | 8.3    | 74.53| 0.77 | 2.43 | 22.08 | 0.09 |
| BACW   | 1.7         | 19.8         | 69.2             | 9.2    | 73.22| 0.79 | 2.24 | 23.43 | 0.12 |
| BACR   | 1.8         | 17.5         | 69.7             | 11.0   | 74.44| 0.67 | 2.22 | 22.57 | 0.10 |
| CACW   | 4.3         | 11.8         | 72.3             | 11.6   | 76.39| 1.21 | 3.34 | 18.63 | 0.43 |
| CACC   | 2.5         | 10.3         | 78.1             | 9.1    | 83.74| 0.69 | 0.67 | 14.72 | 0.74 |

* By difference

3.1.2. Porous structure and physical morphology. The surface areas and pore properties of different ACs were characterized by N$_2$ adsorption and desorption isotherms and the results were showed in Table 2. It could be seen that BACM had the biggest total BET surface area of 911.39m$^2$/g, which was next to BACW, CACW and BACR but much higher than CACC, whose total BET surface area of CACC was 467.34m$^2$/g accounting for about half of that of BACM. The order of total pore volume shared the same trend with total BET surface area. The BACM also had the biggest micropore area followed by BACR, BACW, CACW and CACC, likewise, the micropore volume was also in this order. The sequence of average pore diameter was in the order: BACW<BACR<CACW<BACM<CACC. It was worth mentioned that BACW with the second biggest total BET surface area had the smallest average pore diameter, while the total BET surface area of BACW was bigger than that of BACR but the latter possessed bigger micropore area and average pore diameter than that of the former.

### Table 2. Surface areas and pore structural properties of different activated carbons.

| Samples | Total BET surface area (m$^2$/g) | Micropore area (m$^2$/g) | Total pore volume (cm$^3$/g) | Micropore volume (cm$^3$/g) | Average pore diameter (nm) |
|---------|---------------------------------|--------------------------|------------------------------|----------------------------|---------------------------|
| BACW    | 843.22                          | 572.19                   | 0.56                         | 0.37                       | 2.49                      |
| BACR    | 789.16                          | 596.25                   | 0.45                         | 0.34                       | 3.08                      |
| BACM    | 911.39                          | 687.05                   | 0.65                         | 0.49                       | 3.16                      |
| CACW    | 807.23                          | 423.67                   | 0.48                         | 0.25                       | 3.14                      |
| CACC    | 467.34                          | 295.98                   | 0.30                         | 0.19                       | 4.21                      |

The SEM images of CACs and BACs with ZnCl$_2$ activation or without ZnCl$_2$ activation derived from three straws were showed in Fig.2. The results indicated the surface physical morphology varied with the types of BACs, the pore shapes of three kinds of BAC0s without ZnCl$_2$ activation were regularly tube-like, after ZnCl$_2$ activation, the pristine pore structures were destroyed and many new poles were rebuilt, and the pore shapes and sizes of that became irregular. Those various sizes and shape pores might affect the mass transfer exerting great influence in adsorption processes to impact
the adsorption performances of BACs to some degree considering that an adsorbate molecule should preferentially pass through the superficial pores before arriving at the adsorptive site[12].

Figure 2. SEM of different ACs. (a) BACW0, (b) BACM0, (c) BACR0, (d) CACW, (e) CACC, (A) BACW, (B)BACM, (C)BACR, 5000 multiplier.

3.1.3. Surface chemistry characteristics. FTIR analysis was used to investigate the possible functional groups on the surfaces of different ACs including BACs and CACs (Fig.3), and the result displayed these ACs presenting some similar shapes, manifesting that they shared some similar functional groups on their surfaces. The broad peaks of ACs located at 3400-3437cm⁻¹ were characteristic of hydroxyl or phenolic stretching vibration[27-28]. The bond observed at 2365 cm⁻¹ was ascribed to combination and overtone vibrations of nitrato species[29]. The peak of BACM at 1560cm⁻¹ was related to -NO₂ or -NH[12, 30], and the bond located at about 1410cm⁻¹ could be assigned to C-O vibration in the carboxylate groups[31]. The adsorption bands between 1000 and 1100cm⁻¹ were also discernible on ACs, suggesting that bidentate sulfates existed[30, 32]. In conclusion, there were mainly hydrophilic groups such as -OH, -NO₂, -NH and bidentate sulfates on the surfaces of the BACs and CACs. The hydrophilic groups could promote the adsorption of HCHO[33], therefore, the ACs owned the most affluent hydrophilic groups promoting its adsorption performance to some degree. It was worth mentioning that the adsorption at ambient temperature in this work was main physical adsorption so these functional groups might have part influence on the adsorption performance but they would bring a better benefit at higher temperature when chemisorption played a greater role[34].
3.2. Adsorption performances of the samples

3.2.1. Effect of activating agent (ZnCl₂). To investigate the influence of activating agent (ZnCl₂), BACM0 and BACM with different mass ratio of activating agent (ZnCl₂) and RPm were prepared to compare their adsorption performances, and the results were presented in Fig.4. Compared to the adsorption performance of BACM0, BACM exhibited much better performance, indicating ZnCl₂ activation promoted HCHO adsorption vastly. This could be explained by the enormous improvement of physicochemical property due to the activating agent (ZnCl₂), which was confirmed by the results of BET and SEM. The adsorption performance increased with the increase of the mass ratio of activating agent (ZnCl₂) and BPm, but the further increase of adsorption performance became less when the mass ratio of activating agent (ZnCl₂) and RPm increased from 1.5 to 2. From an economic point of view, the mass ratio of activating agent (ZnCl₂) and BPm of 1.5 could be chosen in the subsequent work and in the potential actual use.
Fig. 5 illustrated the effects of activation temperature and activation time on adsorption performances of HCHO over BACM. As shown in Fig. 5a, E increased with the increase of activation temperature when it was below 750℃, with a tremendous increase from 450℃ to 550℃, and then E yielded a downward trend as the activation temperature further increased to 850℃. It was easy to understand that E was in consistent with the surface areas and pore properties to a great extent, indicating that the surface areas and pore properties improved from 450℃ to 750℃ and then declined from 750℃ to 850℃, therefore 750℃ was the optimal activation temperature. The decline was attributed to the shrinkage of the BAC structure and the sintering effect of the volatiles, resulting in the closing-up and narrowing of the pores[35]. This similar phenomenon was also observed in other work[31]. Qiu et al.[31] thought that increasing activation temperature at lower temperature range could enhance the dehydration of ZnCl2 resulting in a more effective activation, but higher activation temperature might lead to over activation and aggrandize evaporation of ZnCl2. As could be seen from Fig. 5b, the adsorption performance improved with the extension of activation time, and there were two enormous increase from 0.5h to 1h and from 1h to 2h, while the increase from 2h to 3h was inapparent. The phenomena indicated activation times of 0.5h and 1h were insufficient to produce optimal surface areas and pore properties for HCHO adsorption and the activation time of 2h was ample to some degree. This was also consistent with Lua et al.[35], they confirmed that both BET surface area and total pore volume increased with the increase of activation time because of the increasing release of volatile matter, however, they would descend with further prolonging activation time when softening of the volatile took place and closed up some pores, decreasing the BET surface area and total pore volume. Therefore, the activation temperature of 750℃ and the activation time of 2h were chosen in the subsequent study.

Figure 4. Effect of the mass ratio of activating agent (ZnCl2) and BPm on HCHO removal efficiency of BACM.
3.2.2. Effect of O₂ concentration. It was generally accepted that O₂ could be physisorbed on the surfaces of BACs via dispersive van der Waals forces or chemisorbed via formation a chemical bond. Normally, 6% O₂ was chosen in this work because it was the concentration of O₂ of some industrial tail gases. However, the O₂ concentration of air is about 21% and the O₂ concentration of industrial
waste gases varies with various industries and plants. Thus it was extraordinarily essential to investigate the possible effect of the concentration of O\textsubscript{2} on E of BACM and the results were showed in Fig. 6. The Fig. 6 indicated pure N\textsubscript{2} condition exhibited the best adsorption performance, followed by N\textsubscript{2}+6\%O\textsubscript{2} and N\textsubscript{2}+21\%O\textsubscript{2}. In addition, there was a rise or a sudden decline when O\textsubscript{2} was abruptly removed from the SFG or added to the SFG in preliminary experiments. The phenomena manifested that O\textsubscript{2} had apparently inhibitory effect on the adsorption performance of HCHO and the inhibitory effect increased with the content of O\textsubscript{2}, which was inconsistent with our previous work which indicated that O\textsubscript{2} promoted the catalytic oxidation of HCHO at high temperature\cite{23}, which indicated O\textsubscript{2} had different roles in adsorption and catalytic oxidation. The reason for that might be attributed to competitive adsorption between O\textsubscript{2} and HCHO for limited available adsorption sites\cite{34}.

![Figure 6. Effect of the concentration of O\textsubscript{2} on the adsorption performances of BACs and CACs.](image)

3.2.3. Effect of HCHO concentration. 1ppm HCHO and 30ppm HCHO were selected to investigate that the effect of the concentration of HCHO on the adsorption performances of BACs and CACs, and Fig. 7 presented the results. Overall, the loss rate of adsorption performances of ACs per time unit increased as the increase of HCHO concentration, thereinto, BACM exhibited the slowest decline while CACC possessed the fastest decline. Besides, high HCHO concentration could distinguish distinctly the incipient adsorption performances of different activation ACs, revealing their separate adsorption capacity. BACM invariably owned the best adsorption performance while CACW and CACC always possessed the worst adsorption performances whether the concentration of HCHO was either 1ppm or 30ppm. When the concentration of HCHO was 30ppm, the adsorption performance decreased in the order: BACM, BACW, BACR, CACW and CACC, which was in the same order of the total BET surface areas of ACs, indicating total BET surface areas played an important role for HCHO adsorption. It was well known that adsorption performance might mainly depend on the pore property and surface area of adsorbents. In general, the available adsorptive sites might be fleetly and completely occupied, and afterwards multilayer sorption took place when the adsorbate was abundant. Bansode et al.\cite{36} reported that large surface area signified good adsorption performance for adsorbing organic compounds. Therefore, it was logical that BACM with the biggest total BET surface area and
the biggest micropore area had the best adsorption performance while CACC with the smallest total BET surface area and the smallest micropore area owned the worst adsorption performance. Interestingly, although BACW had bigger total BET surface area and total pore volume than that of BACR, BACR possessed a little better adsorption performance than BACW when the concentration of HCHO was 1ppm. The BACR owned bigger micropore area and bigger percentage of micropore volume (micropore volume/ total pore volume) and bigger average pore diameter. Micropore area and average pore diameter had an impact on adsorbing HCHO due to micropore filling which could occur momentously at relatively low partial pressures\(^{12}\), which might be the reasons for that amusing phenomenon. In summary, the surface area and pore property of adsorbents as well as the concentration of adsorbate could contribute to the adsorption performance.
To further evaluate the adsorption performance and adsorption capacity of different BACs and CACs, breakthrough measurements using 100ppm HCHO about 120.7mg/m³ were conducted to clarify the dynamic adsorption behaviors of HCHO on these ACs (Fig.8). Meanwhile, the typical breakthrough curves gave the evolution of the $\frac{[\text{HCHO}]_{\text{in}}}{[\text{HCHO}]_{\text{out}}}$ ratio as a function of time. The adsorbed HCHO manifolded increasingly and eventually reached the breakthrough point, and $[\text{HCHO}]_{\text{out}}$ increased gradually with the extension of adsorption time, ultimately $[\text{HCHO}]_{\text{out}}$ raised to $[\text{HCHO}]_{\text{in}}(\frac{[\text{HCHO}]_{\text{in}}}{[\text{HCHO}]_{\text{out}}}=1)$ for all ACs. As shown in Fig. 8, the breakthrough times were all more than 20h and followed a descended order: BACM > BACR > BACW >CACW >CACC. The HCHO adsorption capacities on BACM, BACR, BACW, CACW and CACC were 153.4, 136.2, 127.8, 84.3 and 72.4mg/g, respectively. Their adsorption capacities were consistent with correlative surface areas and pore properties, which were also confirmed by many previous studies\cite{12, 27, 37}. Notably, BACM and BACR could maintain excellent adsorption performance even at 15h later under high HCHO concentration, manifesting they have the promising future in actual application.
3.3. Regeneration tests of the adsorbent

It was generally accepted that the use of adsorbent merely transferred adsorbate from the gaseous phase to the solid phase and unavoidably induced a disposal and regeneration problem. In addition, adsorbates could desorb from the surfaces of adsorbents and then caused the security considerations when used in indoors. Consequently, it is indispensable to conduct desorption and regeneration tests to estimate the security and recycled ability of the adsorbent. Previous work indicated thermogravimetric analysis (TGA) was applicable to the study of HCHO desorption[12]. As could be seen from Fig. 9, different ACs owned different desorption peaks. CACC had relatively low desorption temperature while BACs owned the similar higher desorption temperatures. The desorption temperature all above 50℃ could contribute significantly to safety use indoors. All of main desorption peaks existed before 150℃, which implied the mainly desorption reactions were all lower than 150℃ and it was feasible to regenerate saturated ACs by thermal regeneration method with relative low regeneration temperature. It was worth mentioning that this low regeneration temperature was economical and convenient in a practical application.
Saturated BACM was employed to be recycled to further explore the regeneration property of the adsorption by thermal regeneration method as mentioned in experimental setup and procedure. The results were showed in Fig. 10, the removal efficiency of regenerated BACM declined and it decreased more and more significantly with the increase of the number of regeneration frequency. The destruction of hole decreasing the BET to reduce available adsorption sites or the incomplete regeneration might be the reason for that. Thankfully, the decline per time was a very pretty little and the adsorption performance after 1 or 2 regeneration was still better compared with that of original CACC as showed in previous figures, which indicated the regeneration was still significantly meaningful in practical application.
4. Conclusions
In this study, BACs with ZnCl₂ activation derived from agricultural wastes were prepared, the optimal prepared condition was achieved and systemic tests were conducted to appraise the adsorption performances of BACs compared with two commercial activated carbons (CACs). The BACs exhibited prominent adsorption performances at different concentrations of HCHO owing to better surface and pore property. Results showed O₂ had a prohibitive effect on the adsorption performance at ambient temperature. The desorption and generation tests were conducted to estimate the security of the adsorbent and recycle regenerated adsorbent. The results indicated that the adsorbents could be securely used indoors and the regeneration of BACM was affordable and economical by the thermal regeneration method. The adsorption performances after 1 or 2 regeneration were still better compared with that of original CAC from coal. Therefore, the combination of the win-win approach to agriculture wastes and cost saving of HCHO removal which offsets the limited adsorbent capacities of adsorbents is of significant practical interest.

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