

Activated carbon with high mesopore ratio derived from waste *Zanthoxylum bungeanum* branches by KNO_3 assisted H_3PO_4 staged activation for toluene adsorption

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Abstract

Waste *Zanthoxylum bungeanum* branches were used to prepare activated carbon adsorbents with high mesopore ratio by H_3PO_4 staged activation method with adding KNO_3 additive. The prepared activated carbon adsorbents were characterized by SEM, BET, FT-IR, and XRD. The adsorption properties of the prepared activated carbon adsorbents were evaluated by the toluene adsorption/desorption in air. The quasi-first-order, quasi-second-order, and Bangham models were used to fit the obtained toluene adsorption results. The oxidative etching of KNO_3 additive improved the pore-forming ability of the H_3PO_4 activator to enhance the activation pore-forming effects of the selected biomass raw material. The secondary pore-forming effects of K atoms promoted the effective expansion of the pore diameter in the activated carbon preparation process to prepare activated carbon adsorbents with high mesopore proportion. The specific surface area and mesopore proportion of the activated carbon adsorbents prepared by adding KNO_3 additive exceeded $1100 \text{ m}^2/\text{g}$ and 71.0%, respectively, and the toluene adsorption capacity exceeded 370.0 mg/g . The rich mesopore structures can effectively reduce the toluene mass transfer resistance, which can promote the corresponding activated carbon adsorbent to be regenerated by low-temperature (40°C) thermal desorption. The toluene adsorption on the prepared activated carbon adsorbents include surface adsorption and diffusion in pore structures, and the toluene adsorption mechanism is more consistent with the Bangham kinetic model.

Introduction

Activated carbon materials, which have high specific surface area, developed pore structure, and stable chemical properties, are widely used in adsorption, energy storage, catalysis, and other fields (Yuan et al. 2008; Diaz et al. 2016; Orisekeh et al. 2021). The factors that affect the application performance of activated carbon mainly include structural characteristics (specific surface area, pore volume, pore size distribution, etc.) and surface properties (types and surface functional groups content, etc.). Therefore, the control of activated carbon structure and surface properties to obtain superior performance has attracted extensive attentions.

The researchers explored the regulation law of the pore structure and surface properties of activated carbon materials through the preparation methods, processes, activator or additives, and even the use of post-treatment or/and secondary pore-forming measures to achieve good results in different research fields (Gu et al. 2015; Dai et al. 2009; Zhang et al. 2019; Azam et al. 2022). The adsorption performance of activated carbon is obviously affected by its pore structure. The reported research results confirm that high specific surface area is more conducive to H_2 adsorption on activated carbon adsorbent, and its pore size distribution has a direct impact on H_2 adsorption capacity. Although rich micropore structures are more conducive to improving H_2 adsorption capacity, however, high micropore ratio is not conducive to the regeneration of the corresponding activated carbon adsorption performance (Xie et al. 2013a, b). Similarly, the micropore structures of activated carbon materials has a large adsorption energy for volatile organic compounds (VOCs). After heat treatment to remove the oxygen containing functional groups on the activated carbon surface, the micropore volume directly determines the VOCs adsorption capacity and renewable performance of the corresponding activated carbon (Lillo-Ródenas et al. 2005; Do et al. 2002). Kaouah et al. (2013) studied on the activated carbon preparation from waste biomass raw materials confirmed that the activated carbon materials preparation process by H_3PO_4 activation method and the activator dosage has a significant impact on its pore structure. That is to say, the pore size distribution can be controlled by the activation process and H_3PO_4 activator dosage. Zhao et al. (2018) used coconut shell as raw material to prepare biomass activated carbon with pore size distribution concentrated at 0.8 nm. Its pore size is similar to the kinetic diameter of chlorobenzene molecules (0.78 nm). The van der Waals potential field between micropore pore walls overlaps to produce strong adsorption potential fields, thus improving the adsorption performance of the corresponding activated carbon for chlorobenzene molecules. Our previous research found that that the H_3PO_4 activation process combined with “low temperature carbonization—high temperature activation” was used to achieve effective activation and pore-forming of *Zanthoxylum bungeanum* branches raw materials (Zhang et al. 2021). The prepared activated carbon materials have micro/mesopore structures, and the specific surface area and mesopore ratio are $1006.2 \text{ m}^2/\text{g}$ and 65.5%, respectively. The high mesopore ratio is more conducive to the adsorbed toluene desorption to show good recycling performance. Wang et al. (2022) added an appropriate amount of H_2SO_4 into the H_3PO_4 activator to prepare *Zanthoxylum bungeanum* branches activated materials based on the combined H_3PO_4 activation and “low temperature carbonization—high temperature activation” process. The obtained results confirmed that the H_2SO_4 additive can effectively promote the H_3PO_4 activator to penetrate into biomass raw materials and promote activation, and H_2SO_4 promotes the hydrolysis of lignocellulose, thus greatly increasing the specific surface area and micropore ratio of the prepared activated carbons. Their specific surface area micropore ratio can exceed $1458.7 \text{ m}^2/\text{g}$ and 60%, respectively. And the toluene adsorption capacity of the corresponding activated carbon is increased by more than 51.8%. In order to further optimize the pore structure of the prepared activated carbon materials, the *Zanthoxylum bungeanum* branches biomass activated carbons with the specific surface area and micropore ratio of $1290.9 \text{ m}^2/\text{g}$ and 63.4%, respectively, are prepared by the joint H_3PO_4 activation and “hydrothermal—low temperature carbonization—high temperature activation” process. Although the toluene adsorption

capacity can reach 532.9 mg/g, the corresponding activated carbon has poor toluene adsorption cycle regeneration performance (Xie et al. 2022).

At the same time, the oxygen atom of the oxygen-containing functional group on the activated carbon surface can exchange electrons with the p -electron of the aromatic rings to form a chemical bonds, so the oxygen-containing functional groups provide a chemical adsorption site with the activated carbon adsorbent, thus increasing the adsorption capacity of the activated carbon on the mixed gas of benzene, toluene, ethylbenzene and xylene (Molina–Sabio et al. 1996; Gonzalez and Roman 2009). Yu et al. (2018) used HNO_3 oxidation to modify the activated carbon surface, which greatly increased the carboxyl groups content ($0.855 \text{ mmol}\cdot\text{g}^{-1}$) on the corresponding activated carbon surface. The electronic effect between carboxyl groups on the activated carbon surface and acetone molecules enhance the acetone adsorption capacity of the studied activated carbon. After modification with HNO_3 , $\text{NH}_3\cdot\text{H}_2\text{O}$, and NaOH solutions, the increase of oxygen-containing functional groups on the corresponding activated carbon surface can remove π electrons from the activated carbon to weaken the dispersion force between the activated carbon and VOCs molecules, thus weakening the physical adsorption between VOCs molecules and activated carbon to reduce the accumulation of residues in micropores and effectively extend the service life of the activated carbon for VOCs adsorption (Bhat et al. 2021). Although secondary pore-forming or surface modification can effectively control the pore structure and surface properties of the corresponding activated carbon materials, there are problems such as complex process, substantial cost increase, and limited adjustable space of pore structure. Therefore, it is of great academic significance and applicable value for the preparation of activated carbon materials with high-performance by selecting appropriate activation preparation process and additives from raw materials to achieve the control of pore structure and surface properties of the prepared activated carbon materials.

In this study, the waste *Zanthoxylum bungeanum* branches were used as raw materials. Based on H_3PO_4 activation method, an appropriate KNO_3 additives (0.00, 0.10, 0.20, 0.30, 0.40 or 0.50 g) were introduced to prepare composite activator. The prepared activated carbon adsorbents were named KAC00, KAC01, KAC02, KAC03, KAC04, and KAC05, respectively. The prepared activated carbon adsorbents were characterized by scanning electron microscopy (SEM), N_2 low-temperature adsorption/desorption (BET), Fourier infrared spectroscopy (FT-IR), and X-ray diffraction (XRD). The adsorption/desorption performances of the prepared activated carbon adsorbents were evaluated by the adsorption/desorption performances of toluene in air. The toluene adsorption mechanism on the corresponding activated carbon adsorbents was studied by using quasi-first-order, quasi-second-order, and Bangham dynamic models, and the toluene adsorption and renewable performance of the prepared activated carbon adsorbents were also evaluated.

Experimental

Preparation of activated carbon adsorbents

The dried *Zanthoxylum bungeanum* branches were smashed and dried in 60°C constant temperature oven for use. 3.0g *Zanthoxylum bungeanum* branches weighed and added into the measured H_3PO_4 solution according to the mass ratio of 1:6 contained KNO_3 with different dosage (0, 0.1, 0.2, 0.3, 0.4, and 0.5g). The prepared activator mixture solution was diluted with 20 mL of distilled water, the obtained activator mixed with *Zanthoxylum bungeanum* branches raw materials which were immersed at 100°C for 24 h in a constant temperature oven. The pretreated samples are put into a quartz tube and heated to 200°C for 2 h, and then they were heated to 650°C for 3 h at a rate of $10^\circ\text{C}/\text{min}$ in N_2 atmosphere. The obtained samples were cooled and washed with distilled water to neutral. And the obtained samples were named as KAC00, KAC01, KAC02, KAC03, KAC04, and KAC05 based on the KNO_3 additive dosage, respectively. The sample naming rule is that the KAC01 representing the KNO_3 additive dosage in H_3PO_4 activator is 0.1g.

Activated carbon adsorbent characterizations

Scanning electron microscope (SEM)

The surface morphology structures of the prepared activated carbon adsorbents were observed by SEM (FESEM, Hitachi, Japan).

Pore structure analysis (BET)

The specific surface area and pore structure of the prepared activated carbon adsorbents were tested by using a specific surface area analyzer (Bester 3H-2000BET-A). 100-150mg samples weighed and degassed under vacuum at 300°C for 5 h. The degassed samples were transferred to the liquid nitrogen cooling environment for N_2 adsorption/desorption test to obtain the N_2 adsorption/desorption isotherms. The specific surface areas were obtained by BET (Brunauer–Emmett–Teller) method. And the pore size distributions were obtained from the BJH (Barret–Jonah–Halenda) and HK (Horvath–Kawazoe) methods from the adsorption branches of isotherms.

Fourier transform infrared (FT-IR) studies

An infrared spectrometer (Hitachi Infrared Prestige-21, Japan) as used to detect the surface functional groups of the prepared activated carbon adsorbents. The spectral grade KBr is used as diluent, and test range is 400–4000cm⁻¹.

X-ray diffraction (XRD) characterization

X-ray diffractometer (Shimadzu, Japan) was used to detect the crystal structure of the prepared activated carbon adsorbents. The test conditions are working current of 30 mA, working voltage of 40 kV. The diffraction patterns were collected from 20 to 60 ° at a scanning speed of 1 °/min and a scanning step of 0.02 °.

Toluene adsorption/desorption performances test

The toluene adsorption/desorption system includes toluene steam generator, constant temperature water bath, quartz tube adsorber, and gas detection system. The containing toluene mixture gas is produced by blowing air into liquid toluene at 0°C to obtain the toluene concentration of 33800mg/m³. The gas flow rate is control at 20 mL/min. A U-shaped quartz tube adsorber containing 100 mg of adsorbent is placed in a constant temperature water bath at 20°C. The toluene concentration in the inlet and outlet gasses is monitored by an online gas chromatograph equipped with a flame ionization detector (GC7890II, China). The toluene breakthrough time is the time required for the toluene concentration in outlet gas reach 5. % of the inlet toluene concentration. The toluene adsorption equilibrium time is the time required for the toluene concentration in outlet and inlet gasses to be equal. The toluene adsorption capacity can be obtained by integrating the toluene adsorption breakthrough curves using the following equation,

$$q_t = \frac{1}{m} \int_0^t v(\rho_0 - \rho_t) dt \quad (1)$$

Where, q_t represents the adsorption amount of toluene (mg/g). v is the inlet gas volume (m³/min). m is the mass of the used adsorbent (g). ρ_0 represents the toluene mass concentration in the inlet gas at the initial time (mg/m³). ρ_t represents the toluene mass concentration in the outlet gas at time t (mg/m³).

Renewable performance test

Two “adsorption-desorption” cycles were conducted on the studied activated carbon adsorbents at room temperature of 20°C to determine the maximum toluene desorption efficiency at low temperature. And the used samples were heated to 40, 60, 100, 150, and 200°C for the adsorbed toluene molecules thermal desorption to study the renewable performance of the used activated carbon adsorbents. And then, the regenerated activated carbon adsorbents were used to toluene adsorption test to determine the toluene adsorption capacity.

Results And Discussion

SEM characterization

The surface morphology of the activated carbon adsorbents prepared with different KNO₃ additive dosages was analyzed by scanning electron microscopy (SEM), and the results are shown in Fig. 1. It can be seen from Fig. 1 that all the prepared activated carbon adsorbents show obvious porous structure, in which the surface pore structures of the KAC00 and KAC01 adsorbents are relatively sparse and low penetration. The pore structure of the KAC02 adsorbent is more dense and penetrating, and the morphology is relatively intact. A large number of intensive slit like pore structures, which can be obviously observed on the KAC03 and KAC04 adsorbents, are penetrated and connected. A large number of circular pore structures can be observed on the KAC05 adsorbent surface, and obvious pore structures can be found on the original pore wall, which indicates that obvious penetration and connection have occurred between the formed pore structures.

The rich pore structure of the prepared activated carbon adsorbents mainly comes from the activation of H₃PO₄ activator, and its formation mechanism is mainly that the H₃PO₄ activator undergoes three stages of diffusion-hydrolysis-impregnation to form H₃PO₄ biomass crosslinkers with biomass macromolecules, by which the pore structures can be formed by high temperature and final washing (Zuo 2018a; Zuo 2017b). It is not difficult to find that the prepared activated carbon adsorbents formed significantly different surface morphology after adding different dosages of KNO₃ additives in H₃PO₄ activator. The result is mainly attributed to the promotional effects of KNO₃ additives on the activation effects. The affect on the activation effects mainly comes from NO₃³⁻ and K⁺ after adding the KNO₃ auxiliary agent. In the H₃PO₄ environment, NO₃³⁻ can nitrify biomass lignocellulose to a large extent. And nitrification can change the biomass lignocellulose structure to a large extent to reduce the diffusion resistance of H₃PO₄ activator in raw materials, which can improve the impregnation effects of H₃PO₄ activator for the used biomass raw materials (Song et al. 1999). HNO₃ with strong acidity, which has stronger catalytic

degradation ability for lignocellulose than H_3PO_4 , can quickly hydrolyze macromolecular sugars (such as hemicellulose) into small molecular substances. At the same time, NO_3^- has strong oxidation under acidic condition, which can oxidize biomass raw materials or formed carbon atoms at high temperatures to achieve “etching” for the used carbon containing raw materials to achieve pore-forming. Therefore, the introduction of KNO_3 additive will enhance the impregnation and pore forming effects of the H_3PO_4 activator (Zhang et al. 2011).

On the other hand, the participation of K^+ also has significant effect on the high-temperature treatment effects of the studied biomass precursor. K^+ can promote the degradation rate of biomass high glycans in the process of heat (Barta–Rajnai et al. 2018), which indicates that K^+ can also play a catalytic role in the thermal decomposition of high glycans under high temperature. As for the H_3PO_4 activation mechanism described above, the introduction of K^+ can promote the hydrolysis of high glycans to reduce the resistance of H_3PO_4 activator swelling plant fibers to promote the H_3PO_4 deep diffusion in biomass raw materials, which can effectively strengthen the activation of H_3PO_4 activator. At the same time, K^+ ions can be reduced into metal K and insert or migrate into the carbon structure of porous carbon, which will promote the porous carbon to further pore-forming on the formed pore structure to improve the pore-forming ability and simultaneously expand the pore size while (Zhang et al. 2009). However, excessive KNO_3 will result in transitional etching in the process of high temperature pore-forming. Therefore, the surface of KAC05 adsorbent prepared with the largest KNO_3 additive dosage is observed the interconnected pore structure and the traces of pore structure collapse.

BET characterization

The BET technology was used to test the specific surface area and pore structure of the prepared activated carbon adsorbents. According to the obtained adsorption/desorption isotherms in Fig. 2, all the prepared activated carbon adsorbents show type I and type IV binding isotherms with H4 hysteresis loops, which indicated that the prepared activated carbon adsorbents have typical microporous/mesoporous structures (Shi et al. 2020). Among them, the rapid adsorption of N_2 molecules in the low-pressure region can be attributed to the rapid filling of nitrogen in the micropores to form type I isotherms. The medium pressure to high pressure region forms type IV isotherms with a H4 hysteresis loop, which can be attributed to the existence of a narrow fissure like mesoporous structures of the prepared activated carbon adsorbents (Teng et al. 2020; Kumar et al. 2021). The steepness of the abrupt jump section of the adsorption/desorption isotherms can reflect the homogeneity of the mesoporous structure in the studied samples. The larger the adsorption/desorption isotherms change amplitude and slope are, the better the homogeneity of pore size distribution is (Zhang et al. 2021). The studied adsorbent samples have similar adsorption isotherms, which indicates that all the prepared activated carbon adsorbents have highly similar pore structure. It can be seen from the pore size distribution curves of the studied samples in Fig. 3 (a) and Fig. 3 (b) that all the prepared activated carbon adsorbent samples have obvious characteristic peaks in the microporous region (0.8-1.2nm) and mesoporous region (2.0-4.0nm). The result confirms that the prepared activated carbon adsorbents belong to typical micro-mesoporous carbon materials.

It can be seen from Table 1 that all the prepared activated carbon adsorbents have large specific surface area greater than $1000 \text{ m}^2/\text{g}$ and large pore volume greater than $1.5 \text{ cm}^3/\text{g}$. It can be seen from Fig. 4 that the specific surface areas of the prepared sample show a “volcanic type” change trend with the increase of the KNO_3 additive dosage. When a small amount of KNO_3 additive is added into the H_3PO_4 activator, the specific surface area of the prepared activated carbon samples increases, significantly. When the KNO_3 additive dosage is 0.2 g, the prepared KAC02 sample has the maximum specific surface area of $1270.8 \text{ m}^2/\text{g}$. Compared with the KAC00 sample without KNO_3 additive, the specific surface area increase by 24.9%. With the further increase of KNO_3 additive dosage, the specific surface area of the prepared activated carbon samples show a downward trend. It can be seen from Table 1 that the pore diameter of the prepared activated carbon samples prepared by adding KNO_3 additive significantly changes. And the micropore ratio of the activated carbon samples prepared by introducing the KNO_3 additive is significantly lower than that of the KAC00 sample prepared without using KNO_3 additive. The result indicates that some micropores are transformed into mesopores and macropores after using the KNO_3 additive, which increases the proportion of mesopores and macropores. That is to say, the KNO_3 additive plays a good role in etching and pore-enlarging, which is consistent with the reported results about the effect of potassium salt additive on the activated carbon pore structure (Liu et al. 2012). The proportion of micropore volume in the total pore volume of the KAC02, KAC03, and KAC04 adsorbents decreases with the increase of KNO_3 additive dosage, and the average pore size increases with the increase of the KNO_3 additive dosage, which further confirms that some micropores are transformed into mesopores or macropores with larger pore size in the process of the activated carbon adsorbents preparation.

Table 1
Physical parameters of the prepared biomass activated carbon adsorbents

Sample	S_{BET} (m^2/g)	Mesopore ratio (%)	V_t (cm^3/g)	Average pore size (nm)	Mic TMP pore size (nm)	Adsorption quantity (mg/g)
KAC00	1017.2	56.6	1.59	6.25	1.06	337.0
KAC01	1126.9	60.2	1.85	6.58	1.05	365.0
KAC02	1291.1	63.3	1.82	5.62	1.01	367.7
KAC03	1212.1	64.9	1.92	6.34	0.95	374.4
KAC04	1131.7	71.6	1.91	6.75	1.01	363.1
KAC05	1052.3	70.7	1.59	6.02	0.94	325.7

The reasons for the above changes are analyzed. The strong oxidative degradation of lignocellulose by NO_3^- in KNO_3 itself and the promotion of high glycan hydrolysis by K^+ enable the activator to activate raw materials more deeply, thus improving the effect of activating pore forming and promoting the increase of specific surface area. The strong oxidative degradation of NO_3^- to lignocellulose and the promotion of K^+ ions to the hydrolysis of high glycans in the used KNO_3 additive enable the H_3PO_4 activator to activate biomass raw materials at a deeper level, which can improve the activation pore-forming effect and increase specific surface area. On the other hand, K^+ ions have obvious pore-enlarging effect for secondary pore-forming of the prepared activated carbon adsorbents under high temperature. K^+ ions can react with carbon atoms in micropore structures to generate metal K, and excessive metal K vapour can be squeezed into the carbon atoms layered structure for interlaminar secondary activation (Okada et al. 2003; Lillo-Ródenas et al. 2003), which can promote the graphite structure layer spacing to increase and effectively expand pore diameter. When excessive KNO_3 additive is added, the oxidation and catalytic hydrolysis from the used KNO_3 additive are too strong. At the same time, secondary activation will occur on the formed micropore wall resulting in excessive etching, which can result in the penetration and collapse of the formed pore structure to reduce the proportion of micropores and specific surface area of the prepared activated carbon adsorbents.

XRD characterization

The crystal structure of the prepared activated carbon adsorbents was characterized by XRD, and the results are shown in Fig. 5. The high intensity XRD peaks are observed at 24° for all the studied samples, which belongs to the {002} crystal plane of the disordered graphite nano-sheet (Wang et al. 2019). The result indicates that the prepared activated carbon adsorbents have an amorphous carbon structure. The {100} crystal plane XRD peaks attributed to amorphous graphite carbon are observed at 43° , which confirms that the prepared adsorbents have some graphite carbon structure characteristics (Du et al. 2020). The microcrystalline structure represented by {002} and {100} crystal planes is a typical biomass activated carbon microcrystalline structure (Cheng et al. 2021), indicating that the prepared activated carbon adsorbents have a mixture phase from graphite carbon and amorphous carbon. The XRD peak of the {002} crystal plane is much higher than that of the {100} crystal plane, which indicates that the amorphous carbon is the main one. It can be seen that there is no obvious change in the XRD peak positions of the corresponding activated carbon adsorbent samples after adding appropriate amount KNO_3 additive in the H_3PO_4 activator. The result indicates that the KNO_3 additive does not significantly affect the crystal structure of the prepared activated carbon adsorbents.

FT-IR characterization

The prepared activated carbon adsorbents were characterized by FT-IR technology, and the results are shown in Fig. 6. The C-C groups stretching vibration infrared peaks at 700 cm^{-1} , C-O groups stretching vibration infrared peaks at 1200 cm^{-1} , C = C groups stretching vibration infrared peaks attributed to olefins at 1550 cm^{-1} , carbonyl C = O groups stretching vibration peaks at 1650 cm^{-1} , and O-H groups stretching vibration peaks attributed to carboxylic acids, phenols, alcohols or/and adsorbed water at 3400 cm^{-1} are observed for all the studied activated carbon adsorbents (Nakajima and Hara 2012; Gomez-Serrano et al. 1996). Among of them, the obvious infrared peaks are observed at 1550 and 1650 cm^{-1} , which are attributed to the products peaks of pyrolysis and polycondensation of lignocellulose benzene ring structure. The formed two infrared peaks indicates that the raw materials are fully pyrolyzed after high temperature treatment (Cao et al. 2014).

As shown in Fig. 6, all the studied activated carbon samples have same surface functional group type with small changes in the peak intensity. Among of them, the infrared peak intensity of the KAC05 adsorbent is weak, which can be attributed to the activation pore-forming

ability of the H_3PO_4 activator being improved after a large amount of KNO_3 additive was added. Therefore, the lignocellulose in the used *Zanthoxylum bungeanum* branches raw material has been largely catalytic degraded in the impregnation stage to show a low carbonyl infrared peak intensity after high-temperature treatment. In general, KNO_3 additive has little effect on the surface functional groups of the prepared activated carbon adsorbents.

Toluene adsorption/desorption performances test

The toluene adsorption/desorption performances of the activated carbon adsorbents prepared with different KNO_3 additive dosage is evaluated, and the results are shown in Fig. 7 (a) and Fig. 7 (b). It can be seen from the toluene adsorption curves of the studied activated carbon adsorbents in Fig. 7 (a) that the toluene adsorption process includes toluene is completely adsorbed by the adsorbents. The used adsorbents starts to be penetrated by toluene molecules, and the toluene concentration in the gas gradually increases after passing through the adsorption bed to finally reach toluene adsorption equilibrium. The penetration time of the KAC00, KAC01, KAC02, KAC03, KAC04 and KAC05 adsorbents for toluene adsorption is 42.24, 47.26, 49.27, 46.07, 44.18, and 45.39 min, respectively. The toluene saturated adsorption capacity on all the prepared activated carbon adsorbents follows the sequence below, $\text{KAC03} > \text{KAC02} > \text{KAC04} > \text{KAC01} > \text{KAC00} > \text{KAC05}$, which indicates that toluene adsorption capacity showed a “volcanic” type change trend with the increase of the KNO_3 additive dosage. When the KNO_3 additive dosage is 0.3g, the prepared KAC03 adsorbent has the maximum toluene adsorption capacity of 374.38 mg/g. The toluene adsorption capacity increase by 11.1% compared with the KAC00 adsorbent prepared without adding KNO_3 additive. It can be seen from Fig. 5.7 (b) that the toluene desorption process on the prepared activated carbon adsorbents is similar. The toluene concentration in the outlet gas decreases with the increase of desorption time. The toluene concentration reduction rate can reflect the desorption rate of the corresponding adsorbent, and the desorption rate on the studied adsorbents is obviously different. The toluene desorption rate on the KAC03 adsorbent is the slowest, and the time required for C/C_0 to drop to 0.5 is 32.5 min. The adsorbed toluene molecules can fastly desorb from the KAC00 adsorbent, and the time required for C/C_0 to drop to 0.5 was 23.9 min. The toluene desorption curves of all the studied adsorbents tend to be flat after a long time desorption at room temperature and does not drop to 0, which indicates that the toluene complete desorption from the studied adsorbents cannot be achieved at room temperature.

FT-IR results confirm that the prepared activated carbon adsorbents surface exists rich oxygen-containing functional groups, in which the carbonyl groups can generate strong interaction with the π electron on the benzene ring of the toluene molecules. The electron interaction between benzene ring and carbonyl group can form “electron donor-electron acceptor” complex. The interaction can promote the chemical adsorption for toluene molecules on the activated carbon adsorbents surface, which can enhance the toluene adsorption effects (Mattson et al. 1969; Chen et al. 2023). The FT-IR results also confirmed that there was no significant difference in the surface functional groups on the studied activated carbon samples. The result indicates that the difference in toluene adsorption capacity among the studied activated carbon adsorbents should be other factors. BET results confirmed that the specific surface area and pore size distribution of the prepared activated carbon adsorbents were significantly different. The reported relevant research results also confirm that the specific surface area is an important factor affecting the adsorption performance of the activated carbon adsorbent. The large specific surface area can provide more adsorption active sites for gas molecules adsorption, which can be attributed to the large specific surface area promoting more surface atoms on the activated carbon adsorbent in an extremely unbalanced state to show strong adsorption and high surface energy (Su et al. 2021). Compared with the KAC00 adsorbent, the specific surface area of the KAC02 and KAC03 adsorbents increased by 24.9% and 19.2%, and the toluene adsorption capacity increased by 8.9% and 11.1%, respectively. The result further confirmed that the specific surface area of the used activated carbon adsorbents has a direct effect on the toluene adsorption capacity. However, the change of toluene adsorption capacity is not directly proportional to the change of specific surface area. Although the specific surface area of the KAC02 adsorbent is larger than that of the KAC03 adsorbent, the KAC02 adsorbent has low toluene adsorption capacity, and the increase of specific surface area does not completely correspond to the increase of toluene adsorption capacity. The result indicates that there are other factors directly affecting the toluene adsorption performances.

Based on the analysis of pore size distribution of the prepared activated carbon adsorbents, the micropores proportion in the prepared KAC01, KAC02, KAC03, KAC04, and KAC05 adsorbents showed a “volcanic” type change trend with the increase of the KNO_3 additive dosage, which is consistent with the change trend of toluene adsorption capacity. The specific surface area of the KAC05 adsorbent is slightly larger than that of the KAC00 adsorbent, but the KAC05 adsorbent has low micropore ratio and low toluene adsorption capacity. It is hereby confirmed that the micropores of the activated carbon adsorbents play a crucial role in effect the toluene adsorption capacity. The result can be attributed to the fact that the micropores size is closer to the molecular dynamics diameter of toluene molecules. And the van der Waals potential field between the pore walls in micropore structures will overlap to form a strong adsorption potential field, which can enhance the adsorption from the micropores for toluene molecules to ptomote more toluene molecules strongly adsorbed in the micropore structures (Zhao et al. 2018). As previously discussed, the specific surface area of the prepared activated carbon adsorbents increase is mainly attributed to the formation of mesopores after the introduction of the KNO_3 additive. However, the contribution of the activated

carbon adsorbent mesopore structure to toluene adsorption is smaller than that of micropore structure, which can well explain that the toluene adsorption capacity change on the studied activated carbon adsorbents is not significantly affected by specific surface area. The specific surface area and micropore structures jointly affect the toluene adsorption capacity of the corresponding activated carbon adsorbent. High specific surface area and high micropore ratio can effectively improve the toluene adsorption capacity of the corresponding activated carbon adsorbent. In the process of toluene desorption from the studied activated carbon adsorbents, the toluene adsorption capacity is negatively correlated with the desorption rate. In addition, the pore size of the activated carbon adsorbent is also an important factor affecting the toluene desorption rate. The KAC03 adsorbent has the lowest mesopore ratio, which is not conducive to the diffusion of gaseous toluene molecules in the desorption process to restrict the effective desorption of the adsorbed toluene molecules show a slow toluene desorption rate.

Dynamics studies

Adsorption kinetics is an important means to study the adsorption process and adsorption mechanism. Three dynamic models, which include quasi-first-order, quasi-second-order, and Bangham models, were selected for nonlinear fitting of toluene adsorption process on all the studied activated carbon adsorbents.

$$q_t = q_e \cdot \exp(-k_1 \cdot t) \quad (2)$$

$$q_t = k_2 \cdot q_e^2 \cdot t / (1 + k_2 \cdot q_e \cdot t) \quad (3)$$

$$q_t = q_e \cdot \exp(k \cdot t^z) \quad (4)$$

Where, q_t is the toluene adsorbed amount per unit mass of adsorbent at time t ($\text{mg} \cdot \text{g}^{-1}$). q_e is the equilibrium adsorption amount ($\text{mg} \cdot \text{g}^{-1}$). k_1 is the rate constant of the quasi-first-order kinetic model (min^{-1}). k_2 is the rate constant of the quasi-second-order kinetic model ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$). k and z are the rate constants of Bangham dynamic model.

As shown in Table 2, it can be found that the regression coefficient R^2 (> 0.996) obtained by fitting the Bangham kinetic model is the largest compared with q_e and R^2 , and the fitting adsorption capacity is the closest to the actual adsorption capacity, which indicates that the toluene adsorption process on all the prepared activated carbon adsorbents conforms to the Bangham kinetic model. That is to say, the toluene adsorption on the studied activated carbon adsorbents conforms to the adsorption mechanism on the gas-solid interface. It is shown that the pore internal diffusion step is the main rate controlling step for the toluene adsorption on the studied activated carbon adsorbents. The toluene adsorption process on activated carbon adsorbents can be divided into surface adsorption and pore internal diffusion. The pore internal diffusion occurs after toluene molecules are rapidly adsorbed on the activated carbon adsorbents surface in the process of toluene molecules entering the zigzag and interconnected micro/mesopore structures. At this time, toluene molecules need to pass through dense micro/mesopore structures and reach adsorption sites in the internal pore structures through diffusion to reach adsorption equilibrium.

Table 2
Kinetic fitting parameters of toluene adsorption on the prepared biomass activated carbon adsorbents

Sample	Adsorption quantity($\text{mg}\cdot\text{g}^{-1}$)	Quasi-first-order			Quasi-second-order			Bangham kinetic models			
		$q_e/(\text{mg}\cdot\text{g}^{-1})$	k_1	R^2	$q_e/(\text{mg}\cdot\text{g}^{-1})$	k_2	R^2	$q_e/(\text{mg}\cdot\text{g}^{-1})$	k	z	R^2
KAC00	337.0	626.3	0.013	0.992	941.3	1×10^{-4}	0.990	404.9	0.009	1.279	0.997
KAC01	365.0	845.9	0.010	0.993	1359.9	1×10^{-4}	0.993	505.4	0.007	1.262	0.996
KAC02	367.7	1028.6	0.007	0.997	1350.5	1×10^{-4}	0.995	542.1	0.007	1.225	0.999
KAC03	374.4	1028.6	0.009	0.996	1426.7	1×10^{-4}	0.994	485.2	0.007	1.308	0.997
KAC04	363.1	582.8	0.015	0.994	976.0	1×10^{-4}	0.994	430.3	0.010	1.254	0.997
KAC05	325.7	780.6	0.010	0.992	1260.9	1×10^{-4}	0.992	468.2	0.009	1.239	0.996

The Weber-Morris model is selected to further study the intraparticle diffusion mechanism of the prepared activated carbon adsorbent for toluene adsorbing.

$$q_t = k_i \cdot t^{0.5} + A_i \quad (5)$$

t is the time (min). q_t is the toluene adsorption amount at time t (mg/g). k_i is the particle internal diffusion rate constant at stage i ($\text{mg}/\text{g}^{-1}\cdot\text{min}^{0.5}$). A_i is the intercept.

The fitting curves of toluene diffusion in the pore structure of the prepared activated carbon adsorbents is shown in Fig. 9. The toluene adsorption on all the studied activated carbon adsorbents can be divided into three stages. In the first stage, toluene molecules diffuse into the adsorbent bed and adsorb on the outer surface of the used adsorbent. In this stage, the adsorption rate is limited by the outer membrane diffusion, and the specific surface area of the used activated carbon adsorbents is the main effect factor (Lashaki et al. 2012). In the second stage, toluene molecules diffuse within the adsorbents internal pore structures, and the diffusion resistance in the internal pore structures is the main factor affecting the adsorption rate. The third stage is toluene adsorption equilibrium stage, which mainly occurs multi-layer adsorption, mainly affected by the total pore volume and mesopore volume.

The simulation results of internal diffusion on all the studied activated carbon adsorbents are shown in Table 3. It can be seen from Table 3 that the difference of k_1 values of all the adsorbents is small. It means that the membrane diffusion rate on all the adsorbents external surface is basically very similar. The k_2 and k_3 values of the KAC00, KAC01, KAC02, KAC03, and KAC04 adsorbents showed a “volcanic” type change trend, in which the k_2 values (71.15) and k_3 values (18.6) of the KAC02 adsorbent are the largest. It can be seen from the BET results that the k_2 and k_3 values of the studied activated carbon adsorbents show the same change trend as the number of mesopores in the activated carbon samples. The result confirms that the rich mesoporous structure can significantly reduce the diffusion resistance in the pores (Yang et al. 2018), thereby improving the mass transfer rate in the process of toluene adsorption. The k_2 and k_3 values of the KAC05 adsorbent abnormally increased, which can be attributed to the collapse of the overdeveloped mesopore structures of the prepared activated carbon adsorbents to form pore structure with larger pore size. Therefore, a higher mass transfer efficiency is achieved with a smaller number of mesopores in the KAC05 adsorbent.

Table 3
Fitting parameters of toluene adsorption in particle diffusion model on the prepared biomass activated carbon adsorbents

Sample	k_1	k_2	k_3	A_1	A_2	A_3	R^2_1	R^2_2	R^2_3
KAC00	47.02	60.17	8.91	-45.71	104.18	266.71	0.965	0.987	0.946
KAC01	47.65	67.29	10.75	-46.48	144.62	278.75	0.966	0.985	0.970
KAC02	42.56	71.15	18.60	-33.67	178.49	214.48	0.957	0.996	0.948
KAC03	46.41	48.22	15.45	-42.20	-9.67	245.01	0.968	0.968	0.976
KAC04	46.31	38.29	10.85	-36.77	45.55	267.76	0.976	0.973	0.954
KAC05	46.41	64.50	13.33	-42.19	131.65	225.59	0.968	0.985	0.970

Renewable performance test

In order to explore the renewable performance of the prepared activated carbon adsorbents for toluene adsorption. The prepared KAC00, KAC02 and KAC05 adsorbents were selected for the toluene “adsorption/desorption” cycle performances test, the results are shown in Fig. 10. The three studied adsorbents show a significant reduction in toluene adsorption capacity after room temperature desorption. The saturated toluene adsorption capacity of the KAC00 adsorbent decreases from 337 mg/g to 300 mg/g and decreases by 11.0%. The saturated toluene adsorption capacity of the KAC02 adsorbent decreases from 364 mg/g to 269 mg/g and decreases by 26.1%. The saturated toluene adsorption capacity of the KAC05 adsorbent decreases from 325 mg/g to 268 mg/g and decreases by 18.5%. The adsorbents, which have been circularly adsorbed with toluene, are thermally desorbed at different temperatures. The toluene adsorption capacity of the studied adsorbents gradually can recover to the corresponding fresh activated carbon adsorbents with the increase of heat treatment temperature. Among of them, the KAC00 adsorbent can completely recover its adsorption capacity for toluene after heat treatment at 100°C. After heat treatment at 60°C, the KAC02 adsorbent can completely recover its toluene adsorption capacity. The toluene adsorption capacity of the KAC05 adsorbent can be restored to 93.5% of the fresh KAC05 adsorbent after heat treatment at 40°C, and the toluene adsorption capacity can be restored after heat treatment at 60°C. That is to say, the studied activated carbon adsorbents show good renewable toluene adsorption capacity.

The toluene adsorption on the activated carbon adsorbent surface includes physical adsorption and chemical adsorption. The physical adsorption strength is weak and easy to desorb, which is mainly affected by the specific surface area and pore structure of activated carbon adsorbent. The chemical adsorption strength is strong, and the desorption is relatively difficult, which is mainly affected by the adsorption active sites on the adsorbent surface. The toluene capacity decrease of the KAC00, KAC02 and KAC05 adsorbents by room temperature desorption is attributed to the fact that part of adsorbed toluene molecules cannot be completely removed under the action of resistance and adsorption force at room temperature to occupy the adsorption sites on the activated carbon adsorbents. In the process of toluene desorption, the resistance of toluene molecules in the pores to be desorbed includes the chemical bond force caused by chemical adsorption and the diffusion resistance affected by the pore structure. By increasing the desorption temperature, the chemical action between toluene and the studied activated carbon adsorbents surface can be effectively destroyed, while the Brownian motion of toluene gas molecules is promoted to accelerate the diffusion rate of toluene molecules from inside to outside promoting the adsorption capacity of the activated carbon adsorbent to be regenerated (Song et al. 1999).

FT-IR results confirm that the carbonyl and other oxygen-containing functional groups on the activated carbon adsorbent surface can form strong interaction with the aromatic ring *p*-orbit electrons in toluene to form chemical adsorption resulting in the adsorbed toluene molecules being difficult to desorb at room temperature. However, the difference in surface functional groups on the studied activated carbon adsorbents is not significant. Therefore, the factor causing the difference in renewable performance of the studied adsorbents should not be the chemical adsorption caused by surface functional groups. Combined with BET and toluene adsorption results, it was confirmed that the addition of KNO₃ additive significantly changed the pore size distribution of the prepared activated carbon adsorbents, and the mesopore proportion of the KAC02 and KAC05 adsorbents increased to 63.3% and 70.7% from 56.6% and increased by 11.8% and 24.9% compared with the KAC00 adsorbent, respectively. It can be seen that the change of diffusion resistance caused by pore size change is the main reason for the difference in regeneration performance of the studied activated carbon adsorbents. The result is due to that the dispersion force formed by superposition of van der Waals potential field in the pore channel is stronger to enhance toluene adsorption strength when the pore diameter is close to the toluene molecules dynamic diameter in the process of micropore toluene adsorption. Therefore, the van der Waals resistance that needs to be overcome in the process of toluene desorption is greater, which results in poor regeneration performance of the prepared activated carbon adsorbents. On the other hand, the non-desorbable substances in the

micropores are continuously accumulated further limiting the removal of toluene molecules due to the small pore size of the micropores, which results in difficult to desorb of the adsorbed toluene molecules (Lashaki et al. 2020; Hashisho et al. 2007). Compared with micropores, the mesopores have larger pore diameter. The van der Waals resistance that needs to be overcome in the process of toluene desorption is smaller, and it is not easy to block the pores. Therefore, the removal efficiency of toluene in the regeneration process is higher (Feizbakhshan et al. 2021). The mesopore proportion (63.3%) of the KAC02 adsorbent is higher than that of the KAC00 adsorbent (56.6%). The high mesopore proportion of the KAC02 adsorbent is more conducive to rapid desorption of the adsorbed toluene molecules by air purging. Therefore, the used KAC02 adsorbent can be regenerated by thermal desorption at a low temperature (60°C) to show excellent renewable performance. The specific surface areas of the KAC05 and KAC00 adsorbents were 1052.3 and 1017.2 m²/g, and the pore volumes were 1.59 and 1.59 cm³/g, respectively. The KAC05 and KAC00 adsorbents have similar specific surface area and pore volume, while the mesopore proportion (70.7%) in the KAC05 adsorbent was much higher than that of the KAC00 (56.6%) adsorbent. The renewable performance of the KAC05 adsorbent is better than that of the KAC00 adsorbent, which also well proves that the high mesopore proportion plays an important role in the good renewable performance for the activated carbon adsorbents.

Conclusion

The participation of KNO₃ additive with oxidative property can effectively enhance the ability of H₃PO₄ activator to activate waste *Zanthoxylum bungeanum* branches raw materials to prepare activated carbon adsorbents and realize the regulation of the pore structures through the KNO₃ additive dosage. The addition of KNO₃ additive introduced oxidation factors into the selected H₃PO₄ activator, and K atoms can be embedded into the internal structure of lignocellulose, which can promote pore expansion to obtain developed mesopore structures. The activated carbon adsorbent with specific surface area of 1291.1 m²/g and mesopore ratio of 71.6% can be prepared through the regulation of the KNO₃ additive dosage, respectively, and the toluene adsorption capacity can reach 374.4 mg/g. The toluene adsorption on the prepared adsorbent is affected by both surface adsorption and pore internal diffusion, and the toluene adsorption mechanism is more consistent with Bangham kinetic model. The prepared activated carbon adsorbents have abundant hydroxyl and carbonyl groups on their surface. The toluene diffusion resistance in the pore structures and surface functional groups are the main factors affecting the the activated carbon adsorbent renewable performance. The abundant mesopore structures endow the activated carbon adsorbent with good renewable performance. The used activated carbon adsorbent can realize the complete regeneration of toluene adsorption performance by thermal desorption at 60°C, which indicates that the prepared activated carbon adsorbents have good potential application value for VOCs adsorption elimination in air.

Declarations

Ethical Approval

This experiment does not involve animal or human experiments. And the submission was approved by the Chongqing Technology and Business University and all authors.

Consent to Participate

The development of the research work and the writing of the manuscript have been agreed and participated by all the authors

Consent to Publish

The manuscript was published with the consent of all the authors

Author contribution

Hongmei Xie, Na Liu, and Haoyu Wang were responsible for the conception and design for the experiment studies and samples preparation. Na Liu, Haoyu Wang, Jia Zeng, and Shuang Chen carried out toluene adsorption performance tests and data analysis. Hongmei Xie, Na Liu, Haoyu Wang, Jia Zeng, Shuang Chen, and Guilin Zhou performed the characterization measurements and interpretation of results. Shuang Chen and Guilin Zhou supervised the study. All authors discussed the results, co-wrote and edited the manuscript. All authors reviewed and approved the manuscript.

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Competing interests

The authors declare no competing interests.

Availability of data and materials

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

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Tables

Table 1 Physical parameters of the prepared biomass activated carbon adsorbents

Sample	S_{BET} (m^2/g)	Mesopore ratio (%)	V_t (cm^3/g)	Average pore size (nm)	Mic TMP pore size (nm)	Adsorption quantity (mg/g)
KAC00	1017.2	56.6	1.59	6.25	1.06	337.0
KAC01	1126.9	60.2	1.85	6.58	1.05	365.0
KAC02	1291.1	63.3	1.82	5.62	1.01	367.7
KAC03	1212.1	64.9	1.92	6.34	0.95	374.4
KAC04	1131.7	71.6	1.91	6.75	1.01	363.1
KAC05	1052.3	70.7	1.59	6.02	0.94	325.7

Table 2 Kinetic fitting parameters of toluene adsorption on the prepared biomass activated carbon adsorbents

Sample	Adsorption quantity($\text{mg}\cdot\text{g}^{-1}$)	Quasi-first-order			Quasi-second-order			Bangham kinetic models			
		$q_e/(\text{mg}\cdot\text{g}^{-1})$	k_1	R^2	$q_e/(\text{mg}\cdot\text{g}^{-1})$	k_2	R^2	$q_e/(\text{mg}\cdot\text{g}^{-1})$	k	z	R^2
KAC00	337.0	626.3	0.013	0.992	941.3	1×10^{-4}	0.990	404.9	0.009	1.279	0.997
KAC01	365.0	845.9	0.010	0.993	1359.9	1×10^{-4}	0.993	505.4	0.007	1.262	0.996
KAC02	367.7	1028.6	0.007	0.997	1350.5	1×10^{-4}	0.995	542.1	0.007	1.225	0.999
KAC03	374.4	1028.6	0.009	0.996	1426.7	1×10^{-4}	0.994	485.2	0.007	1.308	0.997
KAC04	363.1	582.8	0.015	0.994	976.0	1×10^{-4}	0.994	430.3	0.010	1.254	0.997
KAC05	325.7	780.6	0.010	0.992	1260.9	1×10^{-4}	0.992	468.2	0.009	1.239	0.996

Table 3 Fitting parameters of toluene adsorption in particle diffusion model on the prepared biomass activated carbon adsorbents

Sample	k_1	k_2	k_3	A_1	A_2	A_3	R^2_1	R^2_2	R^2_3
KAC00	47.02	60.17	8.91	-45.71	104.18	266.71	0.965	0.987	0.946
KAC01	47.65	67.29	10.75	-46.48	144.62	278.75	0.966	0.985	0.970
KAC02	42.56	71.15	18.60	-33.67	178.49	214.48	0.957	0.996	0.948
KAC03	46.41	48.22	15.45	-42.20	-9.67	245.01	0.968	0.968	0.976
KAC04	46.31	38.29	10.85	-36.77	45.55	267.76	0.976	0.973	0.954
KAC05	46.41	64.50	13.33	-42.19	131.65	225.59	0.968	0.985	0.970

Figures

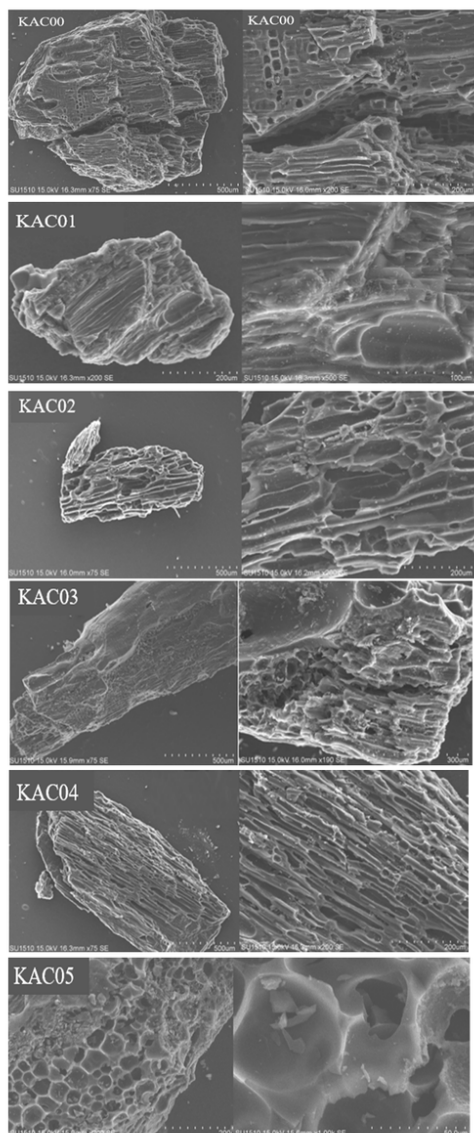


Figure 1

SEM images of the prepared biomass activated carbon adsorbents

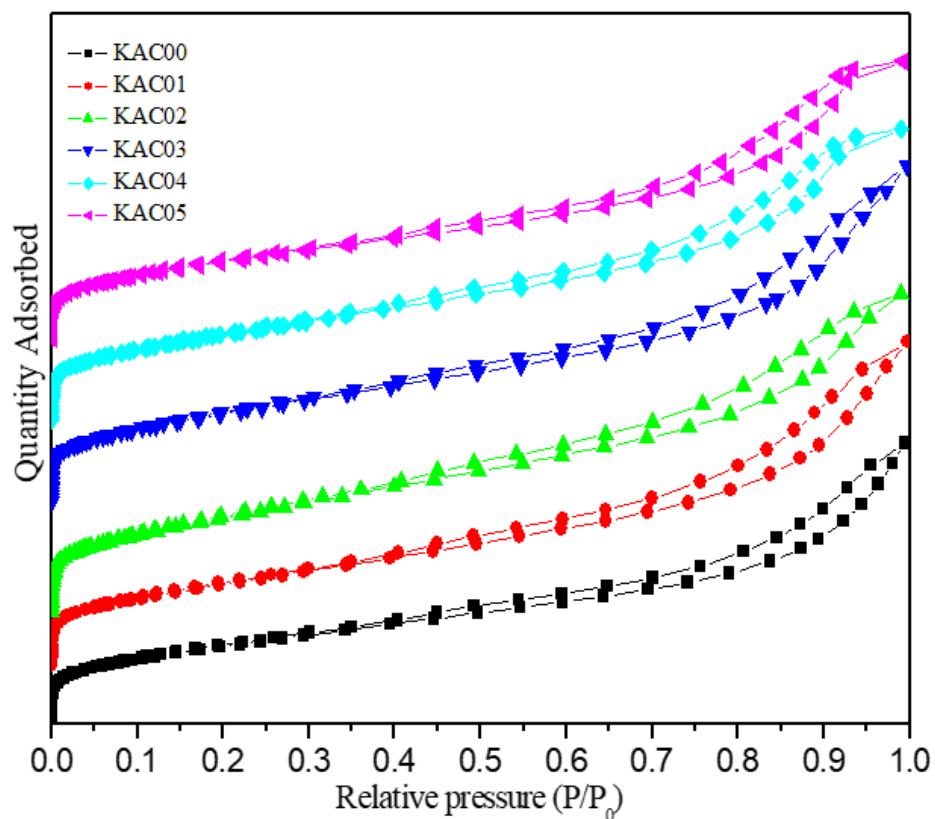


Figure 2

N_2 adsorption and desorption isothermal curves of the prepared biomass activated carbon adsorbents

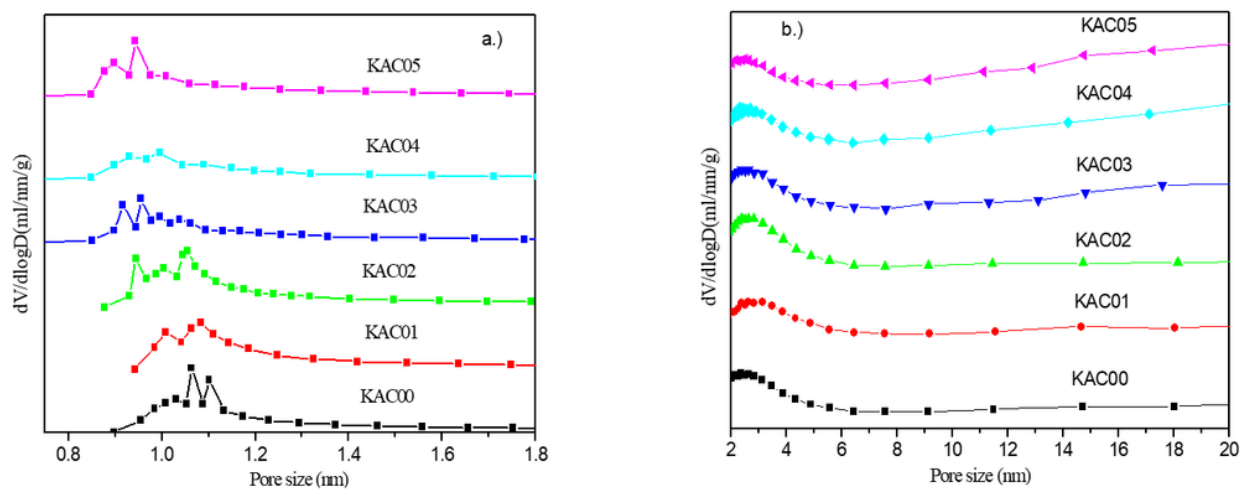


Figure 3

Distribution of (a) microporous (HK) and (b) mesoporous (BJH) of the prepared biomass activated carbon adsorbents

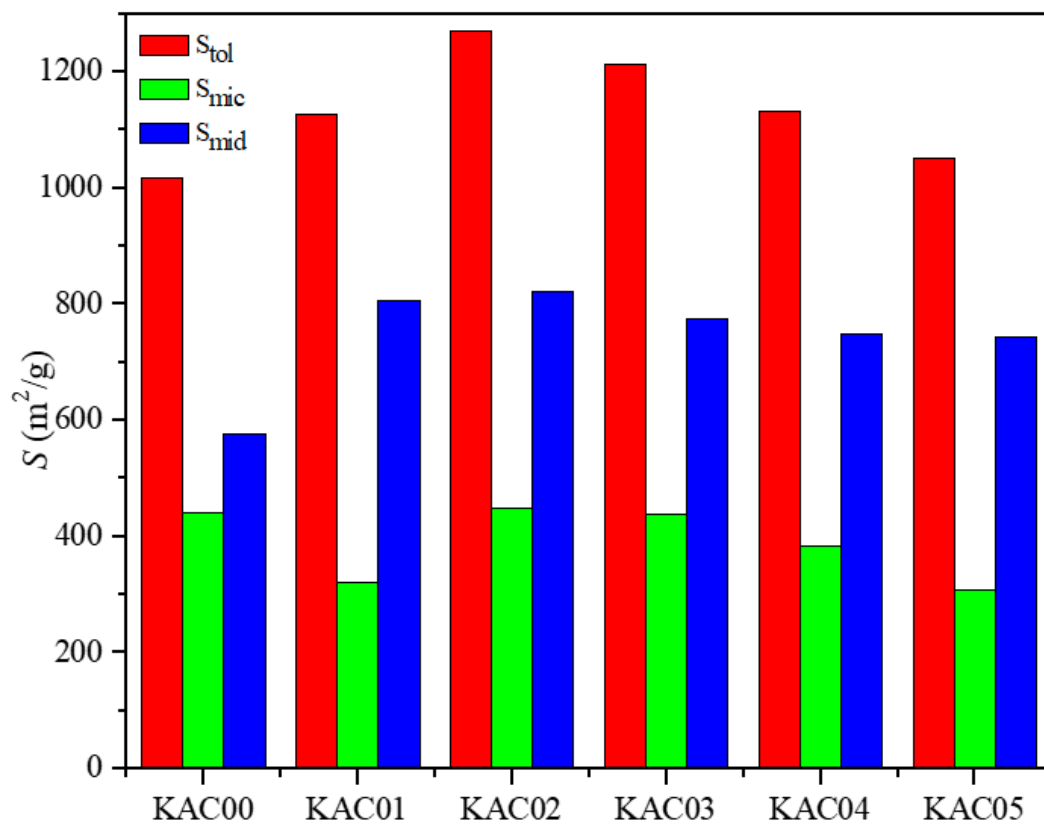


Figure 4

Specific surface area distribution of the prepared biomass activated carbon adsorbents

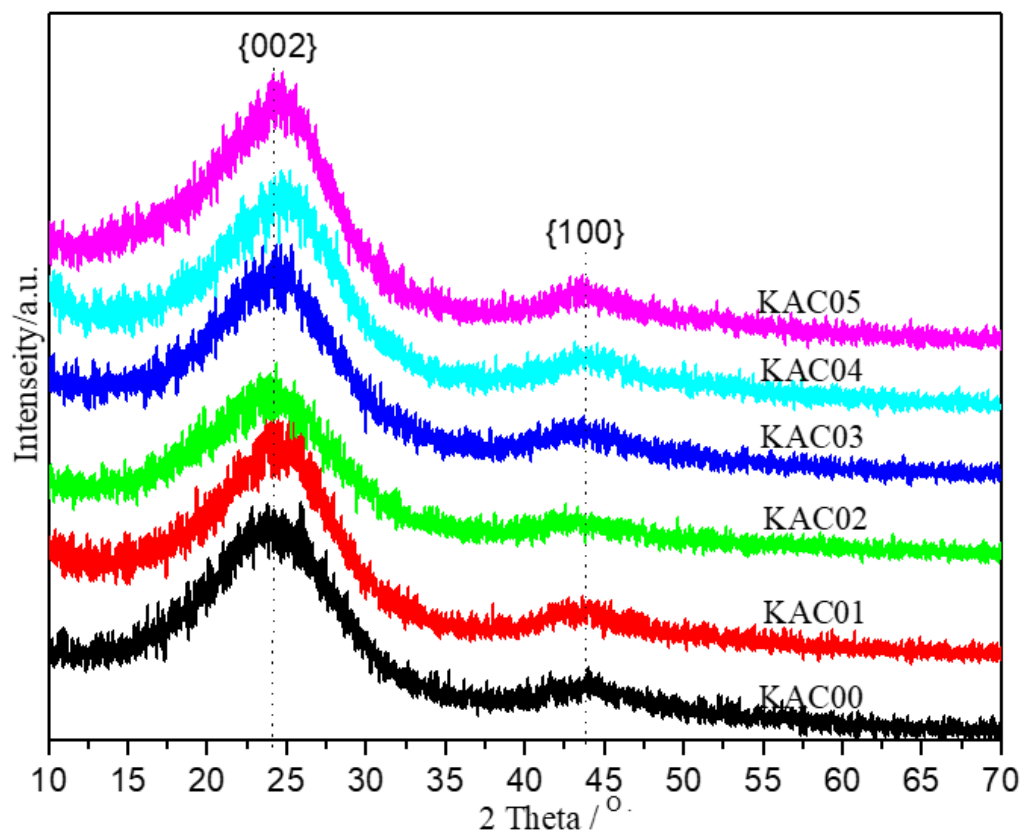


Figure 5

XRD patterns of the prepared biomass activated carbon adsorbents

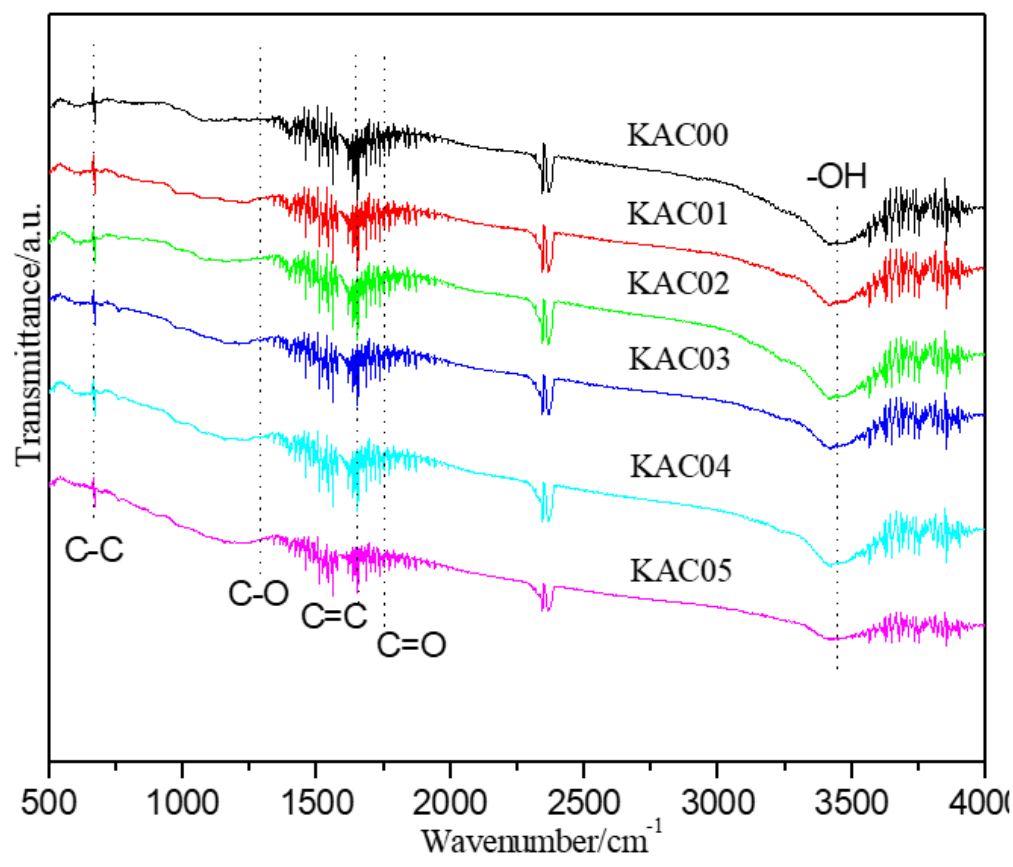


Figure 6

FT-IR spectra of the prepared biomass activated carbon adsorbents

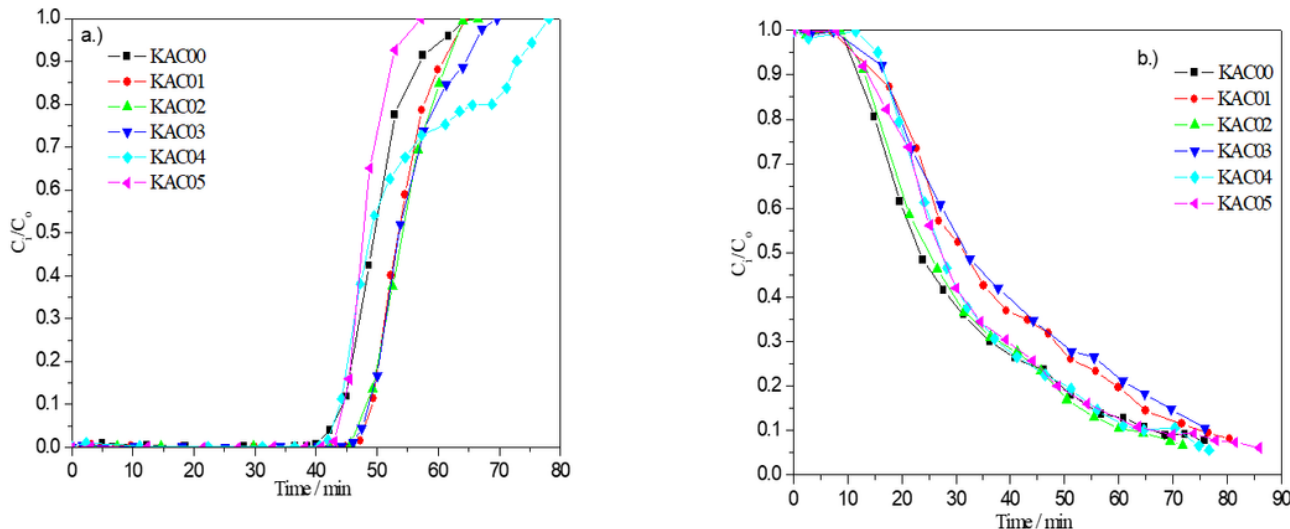


Figure 7

a) Toluene adsorption; b) desorption curves on the prepared biomass activated carbon adsorbents

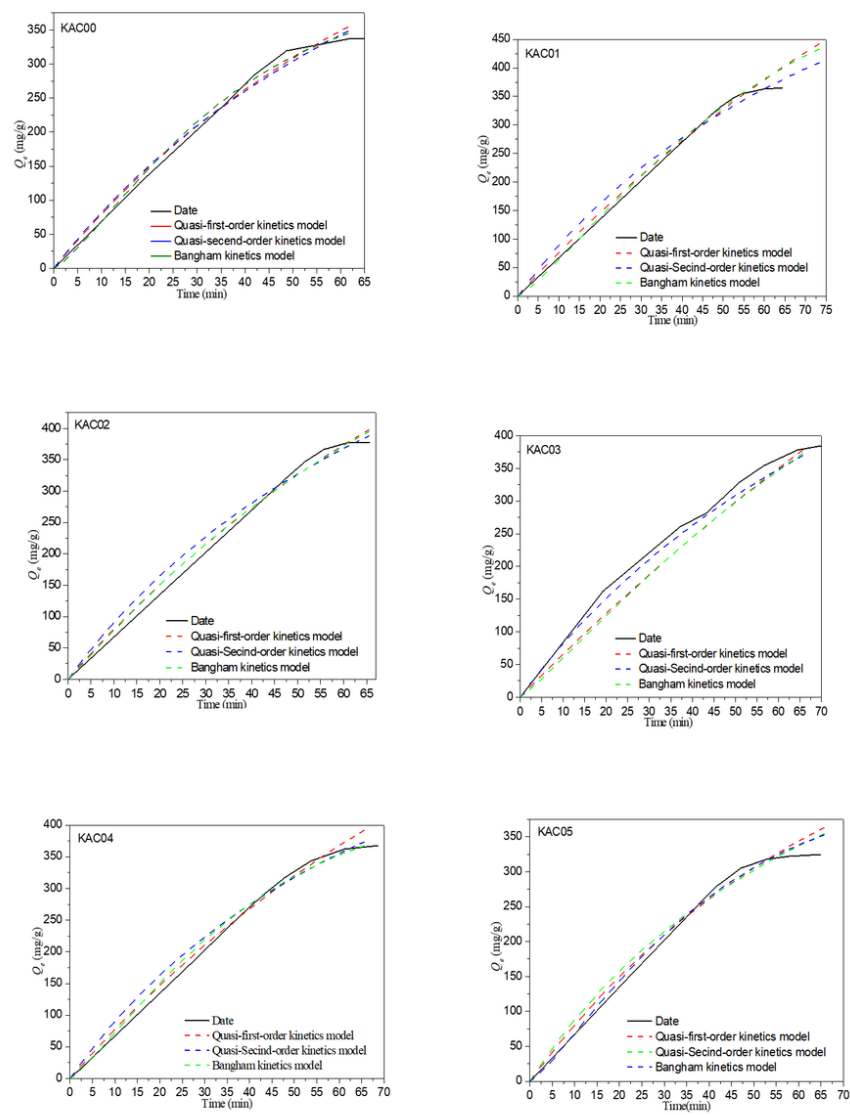


Figure 8
Kinetic fitting curve of toluene adsorption on the prepared biomass activated carbon adsorbents

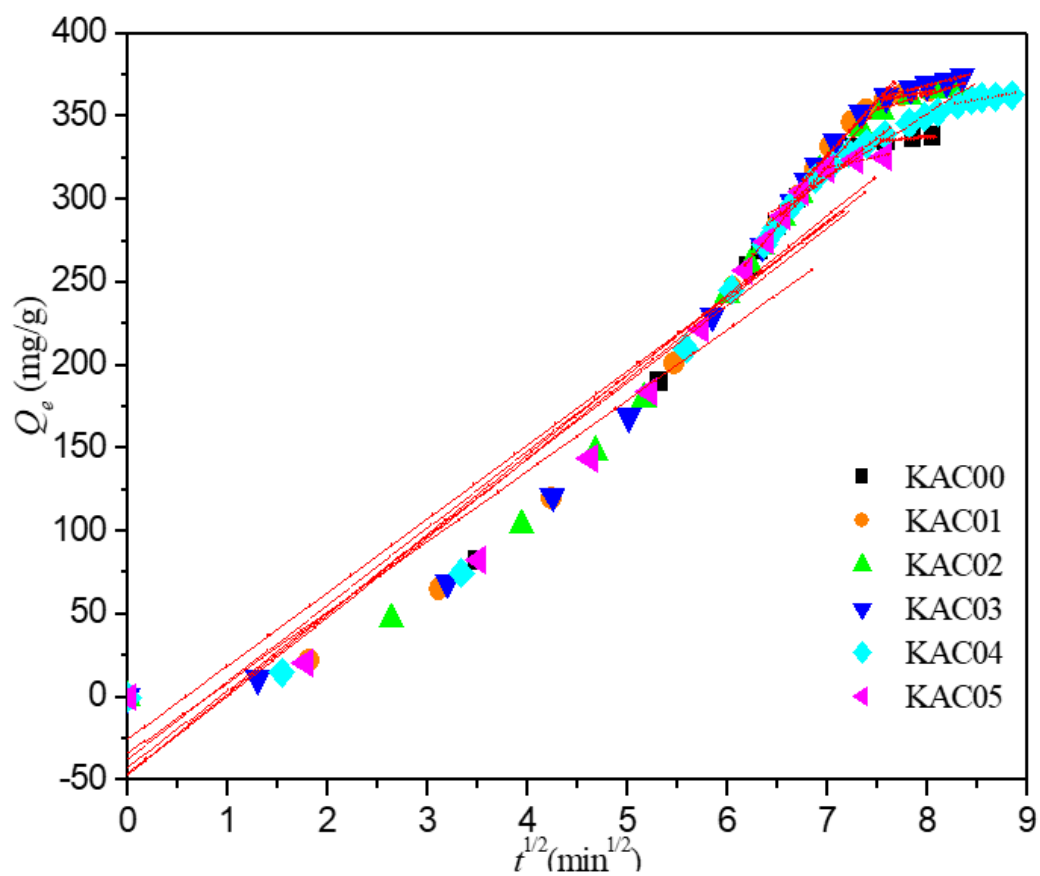


Figure 9

Fitting curves of intraparticle diffusion of toluene adsorption on the prepared biomass activated carbon adsorbents

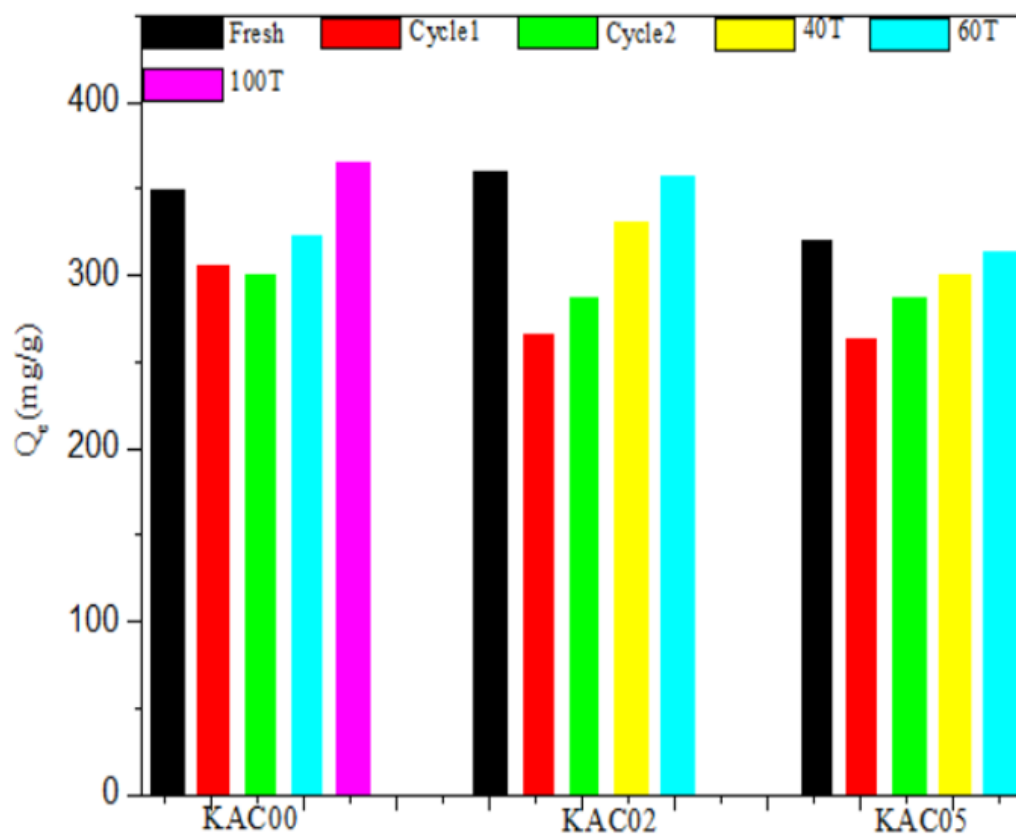


Figure 10

Toluene adsorption/desorption cycle performances on the prepared biomass activated carbon adsorbents