



Performance of sludge-based activated carbon to remove COD from mature landfill leachate: the influence of carburant and activator

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ABSTRACT

This paper describes the preparation of several sludge-based activated carbons (SACs) from sewage sludge with different carburants and activators. A comparative study of COD removal efficiency from the mature leachate by different SACs, and the effects of different carburants and activators on the COD removal performance of SACs are discussed. The results show that COD removal efficiency from the mature leachate by the prepared SACs reaches 72.06% to 85.61%, and the adsorption process was composed of monolayer adsorption and multilayer adsorption, with predominantly multilayer adsorption. The best performance in adsorption efficiency was given by the SAC prepared by using corn stalks as the carburant and $ZnCl_2$ as the activator: a dosage of 2%, adsorption time of 40 min, and pH = 4, led to a COD removal efficiency of 82.25%. Corn straw as the carburant was more positively significant in improving the adsorption performance of SACs: the surface of that SAC was dominated by basic functional groups, and a larger q_L of 227.27 mg/g was obtained, which is 3.68 times that of the SAC prepared with *Brassica oleracea* as the carburant. From the perspective of the activator, $ZnCl_2$ had the best activation effect. Though SAC prepared with K_2CO_3 as its activator obtained the largest q_L of 231.05 mg/g, the apparent adsorption rate was slow, and the adsorption time was much longer than those of the SACs prepared with $ZnCl_2$ and KOH.

Keywords: Sludge-based activated carbon; Mature landfill leachate; Carburant; Activator; COD removal efficiency

1. Introduction

Landfill leachate produced by domestic garbage landfill is a highly concentrated organic wastewater [1], which contains a variety of easily degradable organic compounds and some complex organic compounds [2,3], but it also contains various toxic and harmful substances [4], that can cause serious pollution to water in the environment. Researchers found that humus was the main organic refractory component

of leachate [5,6], and the humus content in leachate has been increasing year by year [7], with ammonia nitrogen and other substances constantly accumulating in the leachate [8]. This will lead to low biological treatment efficiency of the mature leachate, thus greatly increasing the difficulty of treatment. The treatment of mature leachate is a very important social and environmental problem.

At present, a process that uses a combination of biochemical treatment and membrane treatment is widely used in the treatment of leachate in China [9,10]. However,

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with the extension of the operation time of landfill sites, many leachate treatment facilities of landfills cannot meet the environmental protection requirements. The optimization of landfill leachate treatment facilities is an urgent problem to be solved [11]. Researchers believe that a convenient, feasible and economical technical method to improve existing leachate treatment facilities is to add pretreatment facilities [12–14]. Pretreatment of the mature leachate can greatly reduce the pollution load of subsequent membrane treatment, increase the efficiency of membrane treatment and prolonging the service life of the membrane [14]. Activated carbon (AC) adsorption is a relatively economical and effective pretreatment method for high concentration organic wastewater; while reduce the preparation cost and improve the adsorption performance of AC is the key technology.

Sludge-based activated carbon (SAC) can be used as a cheap substitute for commercial activated carbon (CAC) adsorbent [15,16]. As an adsorbent material, SAC has been extensively studied in the adsorption of gases, heavy metal ions and organic pollutants [17,18]. Additionally, compared with the production cost of standard CAC, the total cost of preparing SAC with high adsorption performance is only 5%–10% that of the former [19,20]. Moreover, SAC with carbon as the base, mixed with SiO_2 , CaO , Al_2O_3 , MgO and a variety of transition metals (such as Fe, Mn, Ti), and other inorganic components, can be used as the catalyst or catalyst carrier for catalytic degradation of pollutants, especially organic pollutants. However, the major disadvantage is that the residual components in the process of pyrolysis may block the pores of SAC and some adsorption points [21]. The mineral content in sewage sludge (SS) is high and the pore structure of SAC prepared from SS pyrolysis products is not developed. The specific surface area is also small, usually less than $60 \text{ m}^2/\text{g}$ [22], and the adsorption property is also lower than that of AC prepared from biomass pyrolysis products [21].

Thus, on the one hand, researchers have pretreated the sludge by chemical or physical activation to achieve the purpose of making pores and activating the active site in SAC while, on the other hand, it has been found that increasing carbon content in SS can improve the adsorption performance of SAC. Adding biomass material to SS as the carburant is a technical method that has been proven to be feasible. These biomass forms include corn stalk [23], cotton stalk [24], seeds [25], shells [26], and other agricultural waste [27,28]. The carburants reported in the existing literature are mainly nuts, seeds, and straws, but there have been few studies on leafy vegetables. Generally, leafy vegetables are rich in various organic polymer materials, such as cellulose and lignin, which have been suggested to be primarily responsible for the micro-porosity of AC [29,30].

For this paper, four SACs were prepared as adsorbents, COD removal experiments were carried out on the mature leachate, and the effects of different carburants and activators on the COD removal performance of SACs were discussed. The adsorption experimental data of SACs were fitted by the Langmuir and Freundlich isotherm equations, combined with the thermodynamic curves during the pyrolysis process and analysis of the infrared spectroscopy of the pyrolysis products. The mechanisms of different carburants

and activators affecting the removal performance of SACs also were explored. The conclusion of this article will expand the methods of municipal sludge resource utilization and leachate treatment, so as to achieve the goals of composite governance in treating waste with wastes.

2. Experimental setup

2.1. Feedstock materials

The process for preparing SAC is illustrated in Fig. 1. *Step 1*: The raw materials (such as SS, *Brassica oleracea* and corn straw) were dried at 105°C to constant weight, then crushed and sieved to less than 0.5 mm. The SS and *Brassica oleracea* (B)/corn straw (C) were mixed in the proportion of 3:7 ($m_{\text{SS}}/m_{\text{B/C}}$) as raw materials, which had been proved to be optimal by previous experiments [31,32], and the total weight of the dry mixture basis was 60 g. Then, the above mixture basis was impregnated with activator solution ($w/v = 1:2$) for 24 h and dried at 105°C in an electro-thermostatic blast oven for another 24 h. *Step 2*: The dried impregnated samples were then subjected to pyrolysis at 700°C for 30 min under a nitrogen flow of 100 mL/min, in a stainless steel tank (165 mm \times 50 mm \times 40 mm, ID) within a controlled atmosphere box furnace (QXR1200-30, Shanghai Qian Tong Technology Co., Ltd., Shanghai, China) at a heating rate of $5^\circ\text{C}/\text{min}$. After the pyrolysis process was completed, the furnace was cooled to room temperature under a nitrogen atmosphere. *Step 3*: The carbonized samples were washed with 3M HCl solution for 30 min to remove impurities and ash. Then they were continually washed with hot distilled water (80°C) until the pH of the filtrate was around 7. *Step 4*: The washed samples were dried at 105°C , until a constant weight, to obtain the SAC samples. The parallel experiment was run in triplicate. Table 1 shows the pore structure parameters of SAC samples.

2.2. Adsorption experiments

The mature leachate sample was collected from the storage area of a municipal landfill site that had been operated more than 10 years, in Wuhan, and the municipal landfill site has been sealed since 2018. And then, the storage area of the municipal landfill site was without any treatment. The biochemical properties of leachate were as follows: COD = 2,390 mg/L, $\text{BOD}_5 = 305 \text{ mg/L}$, $\text{NH}_3\text{-N} = 3,619 \text{ mg/L}$ and pH = 8.85. The biodegradability status of the leachate was poor and the value of BOD_5/COD was 0.13. And the adsorption experiments were performed according to previous articles [33].

Adsorption experiments were carried out at room temperature, and the experimental steps were as follows. *Step 1*: 100 mL leachate was accurately measured into a 250 mL flask (with stopper) and an appropriate amount of SAC was added at the designed dosages (0.1–2 g/100 mL leachate). *Step 2*: The pH values of the solutions were adjusted to the appropriate values (2–10) by using a hydrochloric acid buffer or sodium hydroxide buffer. *Step 3*: The covered flask was placed on a constant-temperature oscillation bed, oscillating at a rate of 120 rpm for a designed adsorption time (20–180 min). *Step 4*: After the adsorption experiment, the COD in the supernatant was measured.

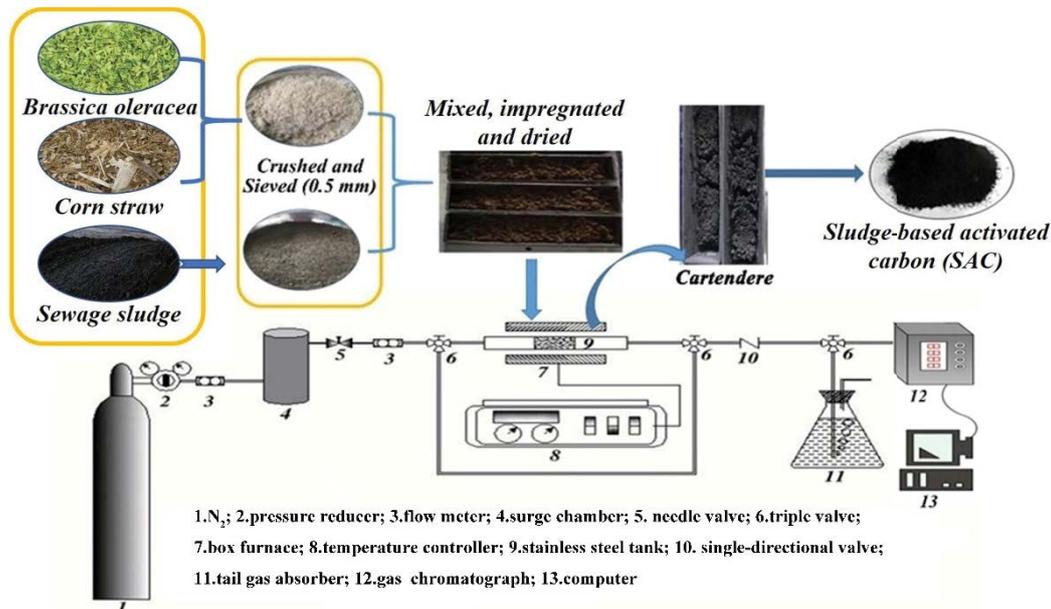


Fig. 1. Process routing and schematic diagram for preparing sludge-based activated carbon (SAC).

Batch static adsorption studies were conducted to investigate the effects of different parameters, including the SAC dosage, adsorption time, and solution pH value, on the removal efficiency of COD from the mature leachate. Under the optimal experimental conditions, the removal efficiency of COD in leachate was studied further. To achieve reliability and reproducibility of the data, adsorption experiments were run in triplicate.

3. Results and discussion

3.1. Effect of carburants on COD removal efficiency from the mature leachate

By studying the effects of SAC-B/ZnCl₂ and SAC-C/ZnCl₂ on the COD removal efficiencies in the mature leachate, the effects of using *Brassica oleracea* leaf and corn stalk as the carburants on the adsorption performance of SACs were compared. Table 2 shows the optimal parameters and the corresponding COD removal efficiencies of the above two SACs.

It can be seen from Table 2 that, under the best parameters, the COD removal efficiencies in the leachate for the two samples are similar, both exceeding 80%. Although SAC-B/ZnCl₂ has a slightly higher COD removal efficiency (3.36% greater), its optimized adsorption time and dosage are higher than SAC-C/ZnCl₂ (i.e., the optimized adsorption time is extended by 25% and the optimized dosage is increased by 50%). Another main difference between the two SACs is the pH value of the adsorption solution: the optimal solution pH value for SAC-B/ZnCl₂ is 8, which is slightly alkaline; while the optimal solution pH value for SAC-C/ZnCl₂ is 4, which is acidic. SAC-B/ZnCl₂ and SAC-C/ZnCl₂ have different requirements for the optimal adsorption environment, which may be caused by the different functional groups on the surfaces of the two SACs [34,35].

Table 3 shows the physicochemical parameters of the two carburants. Although both are agricultural biomass, the *Brassica oleracea* is taken from the leaves of the plant, and the corn straw comes from the stalk of the plant. As shown in Table 3, the physicochemical characteristics of the two

Table 1
Pore structure parameters of SAC samples

Samples	S_{BET} (m ² /g)	V_{total} (cm ³ /g)	D_{ave} (nm)	V_{micro} (cm ³ /g)	I
SC	93.215	0.145	12.509	0.016	0.110
SAC-B/ZnCl ₂	928.222	0.426	5.37	0.017	0.040
SAC-C/ZnCl ₂	901.620	0.469	5.746	0.009	0.019
SAC-C/KOH	462.931	0.367	3.172	0.2318	0.632
SAC-C/K ₂ CO ₃	682.482	0.389	2.467	0.2955	0.7596

S_{BET} : BET surface area; V_{total} : total pore volume; D_{ave} : average pore diameter; V_{micro} : micropore volume; I : microporosity, defined as $V_{\text{micro}}/V_{\text{total}}$; SC, activated carbon prepared using sewage sludge; SAC-B/ZnCl₂, sludge-based activated carbon prepared using sewage sludge and *Brassica oleracea* (B) with ZnCl₂ as activator; SAC-C/ZnCl₂, sludge-based activated carbon prepared using sewage sludge and corn straw (C) with ZnCl₂ as the activator; SAC-C/KOH, sludge-based activated carbon prepared using sewage sludge and corn straw (C) with KOH as activator; SAC-C/K₂CO₃, sludge-based activated carbon prepared using sewage sludge and corn straw (C) with K₂CO₃ as the activator.

Table 2
Optimization parameters of adsorption conditions and COD removal of SACs

Samples	Carburant	Optimum parameters			
		Dosage (g/mL)	Adsorption time (min)	Solution pH	COD removal
SAC-B/ZnCl ₂	<i>Brassica oleracea</i>	3%	50	8	85.61%
SAC-C/ZnCl ₂	Corn straw	2%	40	4	82.25%

Table 3
Physicochemical characteristics of raw carburant

Raw	Proximate analysis (dry basis, wt. %)				Ultimate analysis (wt. %, daf.)					
	Moisture	Volatiles	Ash	Fixed carbon	C	H	O	N	S	
<i>Brassica oleracea</i>	2.96		90.16	1.66	5.18	42.58	5.80	41.44	3.19	0.63
Corn straw	3.24		80.02	2.56	14.18	44.75	5.88	44.86	0.44	1.57

carburants are different: the main variation is that the content levels of volatile matter and fixed carbon are different. These disparities lead to different decomposition processes during the pyrolysis of raw materials, which in turn lead to different compositions of the carbonized surface functional groups during the carbonization stage.

In order to further explore the variations caused by different carburants on the surface functional groups of SACs, the pyrolysis processes of SAC-B/ZnCl₂ and SAC-C/ZnCl₂ and the FT-IR spectra of pyrolysis products, were studied.

Fig. 2 shows the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of (a) SAC-B/ZnCl₂ precursor and (b) SAC-C/ZnCl₂ precursor. It can be seen from Fig. 2 that, although ZnCl₂ was used as the activator for both, the weight loss behaviors of the two were different.

Although the weight loss phenomena of the SAC-B/ZnCl₂ precursor and SAC-C/ZnCl₂ precursor can be divided into three weight loss stages, which are 30°C–100°C, 150°C–450°C and 450°C–600°C [36,37], the weight loss peaks in the DTG profile of the SAC-B/ZnCl₂ precursor appeared at 252°C and 573°C, while the weight loss peaks of the SAC-C/ZnCl₂ precursor appeared at 340°C and 620°C. These differing results indicate that the decomposition temperature of volatiles in the SAC-B/ZnCl₂ precursor was lower.

The optimized carbonization temperatures of SAC-B/ZnCl₂ and SAC-C/ZnCl₂ were, both, 600°C. At this temperature, the weight loss of the SAC-B/ZnCl₂ precursor was 54.24%, while the weight loss of the SAC-C/ZnCl₂ precursor reached 76.42%. Comparing the TG-DTG curves of SAC-B/ZnCl₂ and SAC-C/ZnCl₂, it could be found that the weight loss of SAC-C/ZnCl₂ in the latter two stages was more obvious, indicating that the decomposition was more thorough. It can be inferred that there were more intermediate fragments remaining in the SAC-B/ZnCl₂. Therefore, there are more functional groups on the surface of SAC-B/ZnCl₂ [38].

In order to further identify the composition of the surface functional groups of SAC-B/ZnCl₂ and SAC-C/ZnCl₂, the surface functional groups of the two were characterized by infrared spectroscopy. The absorption bands and peaks of FT-IR spectra provide evidence of the presence of some surface functional groups. Fig. 3 shows the FT-IR spectrograms of the SAC-B/ZnCl₂ and SAC-C/ZnCl₂.

As shown in Fig. 3, the functional groups of both SAC-B/ZnCl₂ and SAC-C/ZnCl₂ showed some oxygen-containing acid functional groups, such as the stretching vibration peaks of the hydroxyl group (O–H) (approximately 3,400 cm⁻¹), stretching vibration peaks for C=C from the aromatic ring structure (approximately 1,600 cm⁻¹), and stretching vibrations of –O– from the lactone groups (approximately 1,100 cm⁻¹) [39,40]. However, the vibration peak intensity of the SAC-B/ZnCl₂ is slightly higher than for SAC-C/ZnCl₂, especially at the stretching vibration peaks of the hydroxyl group (O–H) (approximately 3,400 cm⁻¹). This indicates that the number of oxygen-containing acidic functional groups on the surface of SAC-B/ZnCl₂ is higher than that for SAC-C/ZnCl₂. It can be concluded that the surface of SAC-B/ZnCl₂ is dominated by acidic functional groups, while the surface of SAC-C/ZnCl₂ is dominated by basic functional groups. That explains why the pH value of the optimized adsorption solution of SAC-B/ZnCl₂ is 8, which is slightly alkaline, whereas the pH value of SAC-C/ZnCl₂ is 4, which is acidic. The above results show that different carburants change the surface functional group properties of SACs, which in turn affects the optimal solution pH value of leachate for design of the adsorption process.

The adsorption isotherm of the SACs was drawn under the optimal experimental conditions. The equilibrium isotherms for the adsorption of landfill leachate COD on the SACs are shown in Fig. 4 and the adsorption data were fitted by the Langmuir and Freundlich models.

Fig. 4 shows that the adsorption isotherms of both of the SACs gradually increased as the initial COD concentration of the leachate increased. As shown in Fig. 4a, the adsorption experimental data were fitted by the Langmuir and Freundlich isotherm equations, obtaining R² values of 0.9649 and 0.9479, respectively. This result indicates that the adsorption behavior of SAC-B/ZnCl₂ on leachate COD can be described by the two models. It could be deduced that there is not only monolayer adsorption but also multilayer adsorption in the adsorption process by SAC-B/ZnCl₂. Additionally, the saturated adsorption capacity (q_L) calculated from the Langmuir isotherm adsorption equation was 61.73 mg/g, which was greater than the maximum equilibrium adsorption amount obtained experimentally.

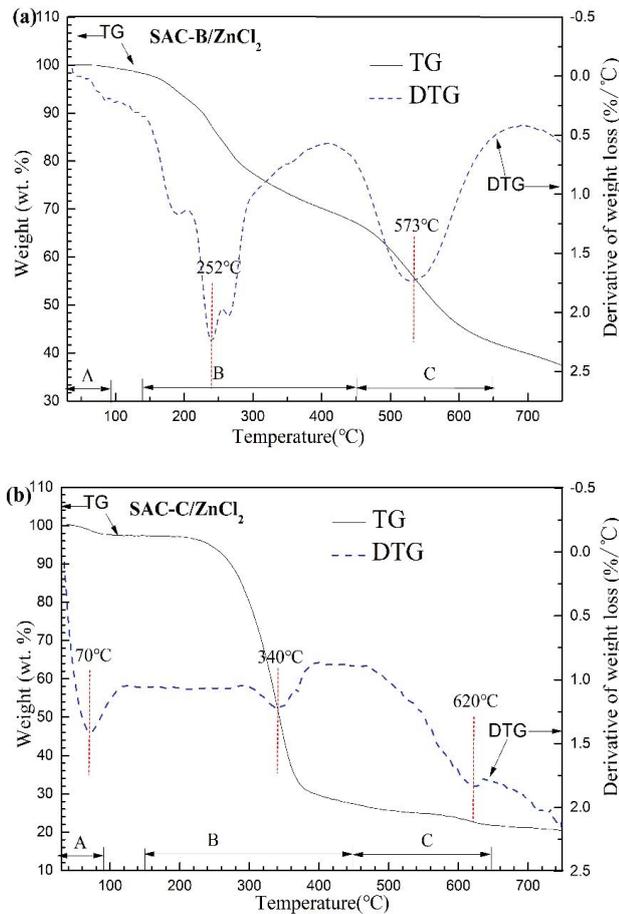


Fig. 2. Thermogravimetric and derivative thermogravimetric curves of the precursors of (a) SAC-B/ZnCl₂ and (b) SAC-C/ZnCl₂.

It was verified that the adsorption behavior of SAC-B/ZnCl₂ was not single monolayer adsorption and that some certain interaction between the SAC-B/ZnCl₂ surface and organic molecules in the leachate could promote the adsorption reaction. The n value of the Freundlich model was 3.76, which indicates that the adsorption of COD by the SAC was mainly multilayer adsorption [41]. Therefore, the Freundlich model provides a more appropriate description. The $1/n$ value of 0.266 could indicate that the adsorption of leachate COD by the SAC occurred easily [42]. The Freundlich isotherm assumes that there is an exponential distribution of adsorption sites and energies, and the multilayer adsorption of the solute occurs on a heterogeneous surface [35].

It can be seen from Fig. 4b that the COD adsorption behavior of SAC-C/ZnCl₂ in leachate can also be described by Langmuir and Freundlich isotherm equations, obtaining R^2 values of 0.9723 and 0.9366, respectively. The q_L calculated from the Langmuir isotherm adsorption equation was 227.27 mg/g. These results indicate that there were uniform binding points and equivalent adsorption energies on the surface of SAC-C/ZnCl₂, which were beneficial to the adsorption capacity for COD, but there was no

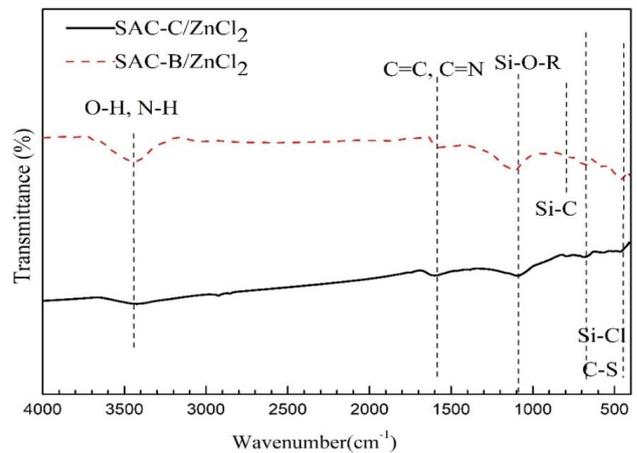


Fig. 3. FT-IR spectra of the SAC-B/ZnCl₂ and SAC-C/ZnCl₂.

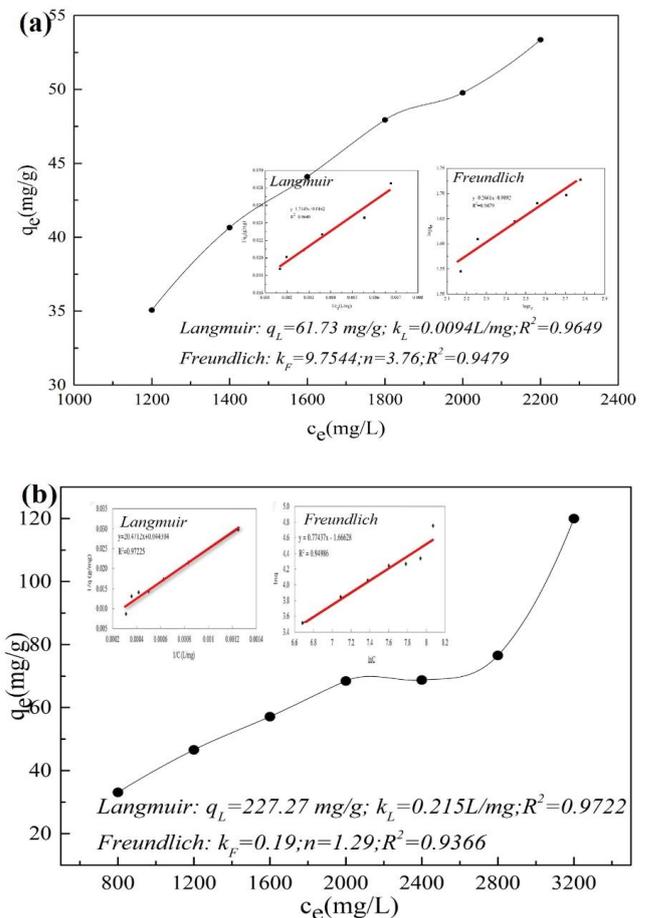


Fig. 4. Equilibrium isotherms for the adsorption of landfill leachate COD on (a) SAC-B/ZnCl₂ and (b) SAC-C/ZnCl₂.

further interaction between the adsorbent and adsorbate [43]. The n value of the Freundlich model was 1.29, which indicates that the adsorption of COD by the SAC-C/ZnCl₂ was mainly multilayer adsorption [41]. And the $1/n$ value of 0.44 could indicate that the adsorption of leachate COD by the SAC-C/ZnCl₂ occurred easily [44].

It can be seen from the above conclusions that the COD adsorption processes of both SAC-B/ZnCl₂ and SAC-C/ZnCl₂ were mainly multi-layer adsorption and the adsorption process occurred easily. However, SAC-C/ZnCl₂ obtained a larger q_L , which is 3.68 times that of the SAC-B/ZnCl₂. Therefore, the use of corn straw as a carburant has a more positive significance in improving the adsorption performance of SACs.

3.2. Effect of activators on COD removal efficiency from the mature leachate

Corn stover was selected as the carburant to study the effect of different activators on the COD removal performance of SACs. By comparing the effects of SAC-C/KOH, SAC-C/ZnCl₂ and SAC-C/K₂CO₃ on the COD removal efficiencies in the mature leachate, the effects of KOH, ZnCl₂ and K₂CO₃ as activators on the adsorption performances of SACs were studied. Table 4 shows the optimal parameters and the corresponding COD removal efficiencies of the above three SACs.

It can be seen from Table 4 that the adsorption performance of SAC-C/ZnCl₂ was the best among the three SACs: with the lowest dosage (2%) and less adsorption time (40 min), the best COD removal efficiency (82.25%) was achieved. Taking adsorption time as the comparison object, the optimal adsorption time of SAC-C/K₂CO₃ was 80 min, which was twice as long as the adsorption time of the other two SACs, yet the COD removal efficiency of SAC-C/K₂CO₃ was the lowest among the three.

It can be seen from Table 1 that SAC-C/ZnCl₂ had the largest surface area (S_{BET}) and average pore size (D_{ave}), and the lowest microporosity (I , defined as $V_{\text{micro}}/V_{\text{total}}$), while SAC-C/K₂CO₃ had the smallest D_{ave} and the highest I . The result verified that the adsorption efficiency of SAC for organic matter was related to the surface pore structure characteristics of the adsorbent, that is, SAC with relatively rich mesoporous structure has higher adsorption efficiency for macromolecular organic materials [34].

It can also be seen from Table 4 that the optimal solution pH value for SAC-C/KOH and SAC-C/ZnCl₂ was similar, which was 5 and 4, respectively; the initial environmental pH value became acidic in the mature leachate; whereas, the optimal solution pH value for SAC-C/K₂CO₃ was 10, which was an alkaline environment.

Fig. 5 shows the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of (a) SAC-C/K₂CO₃ precursor and (b) SAC-C/KOH precursor. The above two activators were potassium-containing compounds, and the weight loss behavior of the two samples was different

from that shown in Fig. 2(b) with ZnCl₂ as the activator. It can be seen from the curves that the SAC-C/K₂CO₃ precursor and SAC-C/KOH precursor had two weight loss peaks in the pyrolysis stage. The first weight loss peak was at 50°C and the second weight loss peak was at 310°C and 250°C, respectively. Comparing the TG-DTG curves of the three samples indicates that potassium-containing activator can accelerate the decomposition rate of organic matter in raw materials, and the acceleration effect of KOH was more obvious.

The surface functional groups of SAC-C/K₂CO₃ and SAC-C/KOH were characterized by infrared spectroscopy, and the FT-IR spectrograms are shown in Fig. 6. As shown in Fig. 6, the infrared spectra of SAC-C/K₂CO₃ and SAC-C/KOH were significantly different. The absorption peaks that were observed for the SAC-C/K₂CO₃ were more in number and more obvious in peak intensity: it merits mentioning that the infrared spectra of SAC-C/K₂CO₃ contained new absorption peaks at 100–1,200 cm⁻¹; 1,300–1,400 cm⁻¹ and 2,700–3,000 cm⁻¹; also, the intensity of the absorption peaks at 1,500–1,600 cm⁻¹ and 3,300–3,500 cm⁻¹ were higher than those for SAC-C/KOH. That dramatic phenomenon proved that the number and content of oxygen-containing acidic functional groups in the surface functional groups of SAC-C/K₂CO₃ were higher than those in SAC-C/KOH, and the functional groups on the surface of SAC-C/K₂CO₃ were mainly acidic functional groups, which explains why the optimal solution pH value for SAC-C/K₂CO₃ was 10.

In conclusion, different activators have varying impacts on the surface pore structure and surface functional groups of SACs, which lead to the differences in the corresponding COD removal efficiencies: the effect on the pore structure distribution leads to the difference in the adsorption time, and the effect on the surface functional groups leads to the difference in the initial optimal solution pH value.

The equilibrium isotherms for the adsorption of landfill leachate COD on SAC-C/K₂CO₃ and SAC-C/KOH is shown in Fig. 7, and the adsorption data were fitted by the Langmuir and Freundlich models.

As shown in Fig. 7a, the adsorption experimental data of SAC-C/K₂CO₃ were fitted by the Langmuir and Freundlich isotherm equations, and the obtained R^2 values were 0.9649 and 0.9479, respectively. This result shows that the adsorption behavior of SAC-C/K₂CO₃ on leachate COD can also be described by the two models. It also indicates that, identical to the aforementioned SAC-B/ZnCl₂ and SAC-C/ZnCl₂, there was not only monolayer adsorption but also multi-layer adsorption in the adsorption process of SAC-C/K₂CO₃. Additionally, the q_L calculated from the Langmuir isotherm adsorption equation was 231.05 mg/g, which was greater

Table 4
Optimization parameters of adsorption conditions and COD removal rate of sludge-based activated carbons (SACs)

Samples	Activator	Optimum parameters			
		Dosage (g/mL)	Adsorption time (min)	Solution pH	COD removal
SAC-C/KOH	KOH	4%	40	5	81.58%
SAC-C/ZnCl ₂	ZnCl ₂	2%	40	4	82.25%
SAC-C/K ₂ CO ₃	K ₂ CO ₃	3.6%	80	10	72.06%

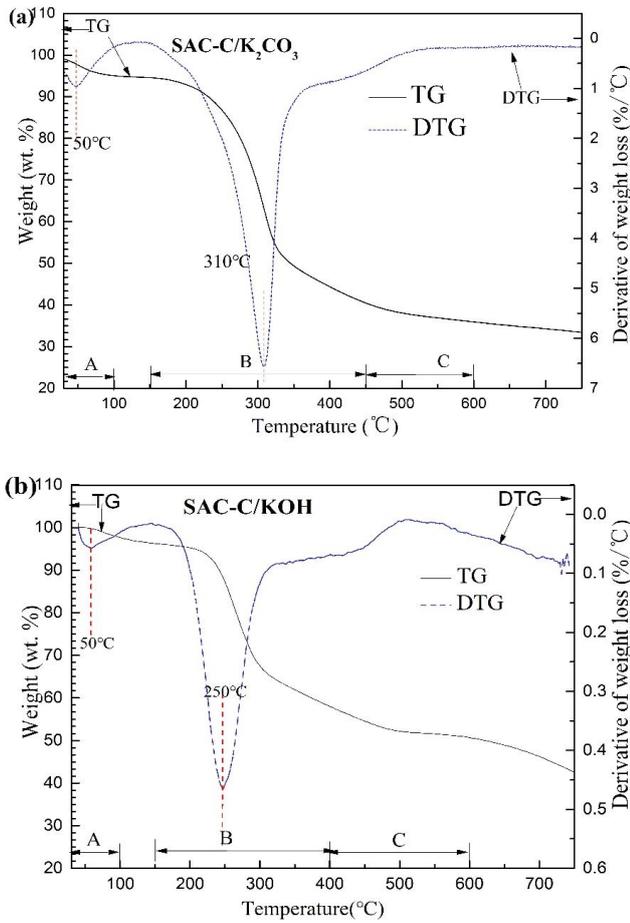


Fig. 5. Thermogravimetric and derivative thermogravimetric curves of the precursor of (a) SAC-C/K₂CO₃ and (b) SAC-C/KOH.

than the maximum equilibrium adsorption amount obtained experimentally. And the *n* value of the Freundlich model was 1.04, which indicates that the adsorption of COD by the SAC was mainly multilayer adsorption [41]. The 1/*n* value of 0.965 was higher than the values for SAC-C/ZnCl₂ and SAC-C/KOH. Therefore, the apparent adsorption rate of SAC-C/K₂CO₃ was relatively slow, and the adsorption time was much longer than that for both SAC-C/ZnCl₂ and SAC-C/KOH.

It can be seen from Fig. 7b that the COD adsorption behavior of SAC-C/KOH in leachate can also be described by Langmuir and Freundlich isotherm equations, which obtained *R*² values of 0.9633 and 0.9499, respectively. The *q_L* calculated from the Langmuir isotherm adsorption equation was 44.80 mg/g, which was also greater than the maximum equilibrium adsorption value obtained experimentally. It was verified that the adsorption behavior of SAC-C/KOH was composed of both monolayer adsorption and multilayer adsorption. In addition, the Freundlich equation was used to fit the adsorption process of SAC-C/KOH and the results showed that the *n* value was 1.31. Leng and Pinto [45] believed that the smaller the value of *n* (1 < *n* < 10) obtained, the higher the degree of agreement with the Freundlich equation for the adsorption process. Thus, the adsorption behavior of SAC-C/KOH was mainly multilayer adsorption. Also, the 1/*n* value was 0.763, which was higher

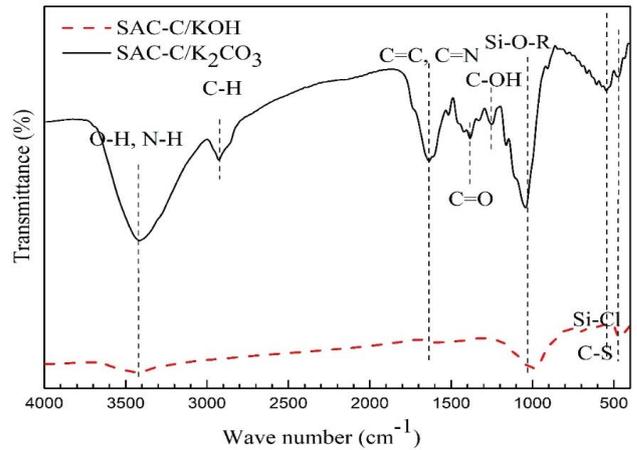


Fig. 6. FT-IR spectra of the SAC-C/K₂CO₃ and SAC-C/KOH.

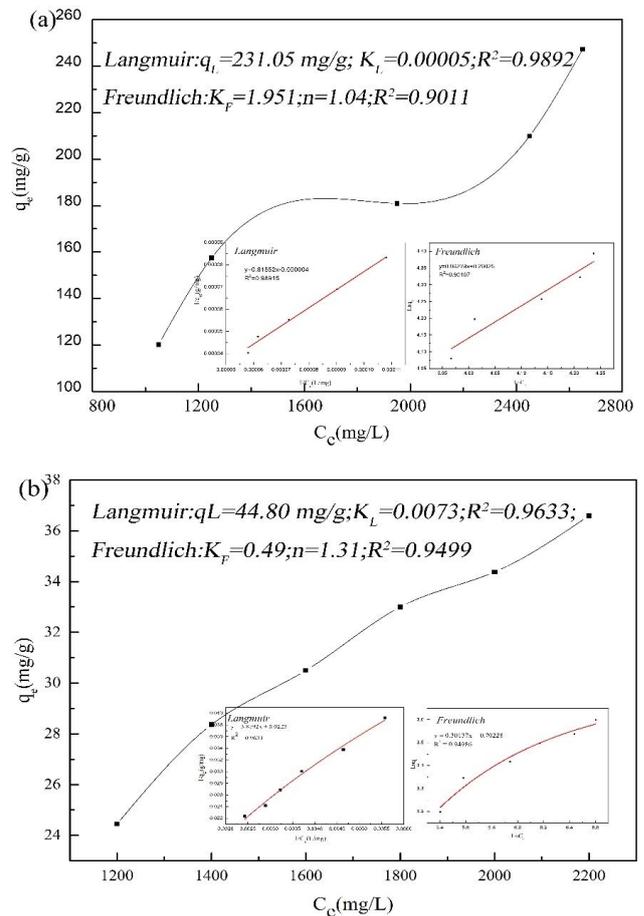


Fig. 7. Equilibrium isotherms for the adsorption of landfill leachate COD onto (a) SAC-C/K₂CO₃ and (b) SAC-C/KOH.

than the value for SAC-C/ZnCl₂, indicating that the adsorption of leachate COD by SAC-C/KOH was more difficult to achieve than that of SAC-C/ZnCl₂. Thus, for the same length of adsorption time, the optimal dosage of SAC-C/KOH was greater than that of SAC-C/ZnCl₂.

4. Conclusions

For this paper, four SACs were prepared as adsorbents, COD removal experiments were carried out on the mature leachate, and the effects of different carburants and activators on the COD removal performances of SACs were discussed. The conclusions were as follows:

- The results showed that COD removal efficiency from the mature leachate by the prepared SACs reached 72.06%–85.61%. The best performance in adsorption efficiency was the SAC prepared by using corn stalks as the carburant and ZnCl_2 as the activator: dosage of 2%, adsorption time of 40 min, $\text{pH} = 4$, and attained COD removal efficiency of 82.25%.
- Corn straw as the carburant demonstrated a more positive significance in improving the adsorption performance of SACs. The surface of SAC-B/ ZnCl_2 was dominated by acidic functional groups, while the surface of SAC-C/ ZnCl_2 was dominated by basic functional groups. The COD adsorption processes of both SAC-B/ ZnCl_2 and SAC-C/ ZnCl_2 were mainly multi-layer adsorption, and the adsorption process occurred easily. However, SAC-C/ ZnCl_2 obtained a larger q_L , which was 3.68 times that of SAC-B/ ZnCl_2 .
- ZnCl_2 as the activator produced the best activation effect for preparing the SAC. Three SACs were prepared with different activators that were composed of monolayer adsorption and multilayer adsorption, with multilayer adsorption being predominant. With the same adsorption time, the optimal dosage of SAC-C/KOH was greater than that of SAC-C/ ZnCl_2 . Although SAC-C/ K_2CO_3 obtained the largest q_L of 231.05 mg/g, the apparent adsorption rate was slow, and the adsorption time was much longer than that of either SAC-C/KOH or SAC-C/ ZnCl_2 .
- The most obvious effect that the carburant had on the COD adsorption process was that it changed the surface functional group properties of SACs, which in turn affected the initial environmental pH value of the mature leachate; the influence of different activators on the pore structure distribution of SACs leads to its influence on the adsorption time, and the influence on the surface functional groups leads to its influence on the initial environmental pH value of the COD removal from mature landfill leachate.

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