Corn cob-derived Activated Carbon for Efficient Adsorption Dye in Sewage

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Abstract

Water pollution is a hot issue in the world today. Therefore, the effective removal of organic pollutants in water has become an urgent problem to be solved. Herein, natural biomass wastes, corncobs as raw materials via a simple carbonization-activation method to prepare corn cob-derived activated carbon (CCAC) for dye adsorption in polluted water. The effects of adsorbent dosage, dye concentration, pH and temperature on adsorption performance were also explored. Benefiting from the large specific surface area ($2308.27 \text{ m}^2 \text{ g}^{-1}$) and abundant micro-/mesoporous structure of CCAC-900-4, it has the large adsorption capacity (523.18 mg g^{-1}) and a high removal rate of 99.52% for MB. Meanwhile, the maximum adsorption capacity of CCAC-900-4 was 864.58 mg g^{-1} by Langmuir isotherm fitting. More interestingly, after five cycles of tests, the removal rate of methylene blue by CCAC can still reach 99.34%. This work provides a simple way for the subsequent high value-added utilization of biomass waste resources.

Keywords: Activated carbon, Dye, Adsorption, Corn cob, Water pollution.

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1. Introduction

With the development of the dye industry and the extensive use in production, the annual discharge of dye effluents brings about many environmental pollution problems and adverse effects on human health, they cause the greenhouse effect, ozone layer depletion and cancer, *etc.*^[1-4] Organic dyes have been widely used as an important industrial raw material in the dyeing and paper industries.^[5,6] To date, the aforementioned type of organic dyes has been used in silk, cotton, hemp, polyester and other fibers.^[7,8] Methylene blue (MB) is an important organic chemical synthetic cationic dye that readily forms monovalent organic quaternary ammonium cationic groups in the aqueous solution.^[9] The deep color and high concentration of MB wastewater has become an important

source of pollution and its resistance to biodegradation, oxidation and photolysis capacity greatly increases the difficulty of treatment. Therefore, it is urgent to find a cost-effective method to treat MB dye wastewater.^[10,11]

Various technologies such as microbial degradation, membrane separation, photocatalysis and advanced oxidation have been used to remove dyes from wastewater in the past decades, but most of these methods have disadvantages such as high cost, high energy consumption, low efficiency, incomplete decolorization and even further presence of toxic sludge.^[12-15] Adsorption method has a broad application prospect in dye wastewater treatment because of its economic and environmental protection, simple operation, low secondary pollution and good overall benefits.^[16] Biochar is a carbon-rich solid that can obtain porous products by pyrolyzing biomass under oxygen-limited conditions. It has the advantages of large specific surface area, developed pore structure, rich oxygen-containing functional groups and many negative surface charges.^[17] Heretofore, biochar is widely used in gas adsorption and separation, heterogeneous catalysis, sensors, energy storage and other fields.^[18-21] Compared with other carbon materials, biochar has a more selective feedstock, and therefore the physical and chemical properties of biochar are quite different. Biochar prepared under a wide variety of

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pyrolysis temperatures, time and activator ratios have different specific surface areas, organic element contents and adsorption efficiencies. In particular, biomass with nitrogen and oxygen functional groups in the skeleton provides a wealth of active sites for the adsorption of specific dyes on biochar.^[22]

Agricultural and forestry wastes such as rice husk, coconut husk, fungus bran, sawdust and peanut shells are renewable and low-cost biomass resources. If these biomass wastes are prepared into biochar for adsorption applications, it will not only greatly reduce the cost of adsorbent preparation, but also benefit to protect the environment. Corn cob is a common biomass waste from agriculture, with a global annual production of about 28 million tons.^[23] How to use corn cobs efficiently is a current research hotspot in the field of processing residuals from agricultural and forestry production. However, most of the current corn cobs are stacked in the open or burnt, which not only causes environmental pollution but also wastes resources. As corn cobs contain a large amount of cellulose, hemicellulose, lignin and various functional groups, activated carbon with high added value can be obtained through carbonization.^[24] To improve the adsorption capacity of biochar for organic dyes, the specific surface area and pore volume must be increased. Whereas, biochar consists mainly of micropores, which are conducive to the adsorption of small molecules, but lacks mesopores, which reduces the mass transfer rate and the adsorption capacity of large organic dyes. Hierarchical porous carbon therefore has great potential for dye adsorption. Micropores have good adsorption capacity for small molecules, while mesopores can adsorb large molecules and are the main transport channel for adsorbents.

Herein, corn cob-derived activated carbon (CCAC) was prepared by a convenient activation-carbonization method, and its adsorption performance on organic dyes was investigated. As a common agricultural and forestry waste biomass, the morphological evolution of CCAC was studied under different conditions of carbonization temperature and activator ratio. The adsorption mechanism and properties of CCACs were investigated by adjusting the types of organic dyes. The macroscopic physical properties (specific surface area, pore volume and element composition) of the prepared CCACs were analyzed. The best obtained activated carbon exhibited a specific surface area of 2308 m² g⁻¹, a total pore volume of 1.21 cm³ g⁻¹ and a mesopore of 0.82 cm³ g⁻¹.

Benefitting from the ultra-high specific surface area and hierarchical porous structure, CCAC has good adsorption capacity for various organic dyes. Additionally, regeneration performance of CCAC was studied by a recycling experiment. Therefore, the synthesis and application of CCACs solve the problem of inefficient treatment of agroforestry waste while realizing the comprehensive utilization of circular economy and verifies the feasibility of advanced treatment of wastewater containing organic dyes.

2. Experimental details

2.1 Materials

Corn cob (CC) from rural Harbin, Heilongjiang province, potassium hydroxide (KOH), sulfuric acid (H₂SO₄), hydrochloric acid (HCl), rhodamine B (RhB), congo red (MR), methyl orange (MO) and neutral red (NR) were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd., China. Crystal violet (CV) was purchased from Tianjin Guangfu Technology Development Co., Ltd., China. Methylene blue (MB) was supplied by Tianjin Yongda Chemical Reagent Co., Ltd., China. The reagents were analytical grade and did not require any further purification or other treatment.

2.2 Preparation of CCAC

The CCAC was prepared using a slightly modified procedure previously published by our group.^[25] First, the corn cob was washed, dried and crushed to corn cob powders, then the corn cob powders were pre-carbonization at 450 °C for 2 h under N₂ protection to obtain the pre-carbonization corn cob carbon (CC). Subsequently, CC and KOH were mixed at a certain mass ratio (CC:KOH mass ratio=1:1~1:5), heated to 700~1000 °C with a heating rate of 5 °C min⁻¹ in N₂ atmosphere and maintained at this temperature for 1 h. Finally, the products are washed with 0.5 M H₂SO₄ solution and deionized water to pH neutral and dried for 12 h at 120 °C to obtain the CCAC-T-m. Where T is the activation temperature and m is the activation mass ratio.

2.3. Dye adsorption using CCAC

The adsorption experiments were carried out by using 5~40 mg adsorbent and 10~250 mg L⁻¹ of MB in 50 mL of a vial in shaker (agitation speed 150 rpm) reaction at 293~313 K. The pH value of the solution was adjusted and maintained during the adsorption process using 1 M NaOH and 1M HCl. After 420 min, 3 mL of the supernatant was taken on a UV-Vis spectrophotometer to measure the residual amount and calculate the adsorption amount. The removal efficiency (%) and adsorption capacity at equilibrium (q_e) be calculated following Eq. (1) and Eq. (2).^[26,27]

$$\text{Removal}(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e) \times V}{M} \quad (2)$$

where C_0 and C_e (mg L⁻¹) are the initial and equilibrium

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Fig. 1. SEM images of (a, b) CCAC-900-4, (c) CCAC-900-1, (d) CCAC-900-2, (e) CCAC-900-3, (f) CCAC-900-5.

concentration of the pollutant, V (mL) represents the volume of the pollutant solution, and M (g) is the mass of the adsorbent and Brunauer-Emmett-Teller (BET) measurement (ASAP 2020, Micromeritics, USA).

2.4. Characterizations

The Fourier transform infrared (FTIR) spectroscopy analysis was characterized by an iS 10 infrared Spectrometer (Thermo Nicolet Co. Waltham, MA, USA) in the range of $400\text{--}4000\text{ cm}^{-1}$. The X-ray diffraction (XRD) patterns were recorded using Rigaku D/Max 2200 with $\text{Cu-K}\alpha$ ($\lambda = 1.5458\text{ \AA}$) source and 40 mA, 40 kV advance diffractometer operating with the range of 5° to 80° with scanning rate of 5° min^{-1} investigate the crystal structure of the samples. The morphologies of resulting samples were characterized by a scanning electron microscopy (SEM) (Quanta 200, FEI, USA). The element of carbon and oxygen in the sample was determined by an X-ray photoelectron spectrometer (XPS) (THERMO Thermoelectric, USA). The specific surface area of these samples was characterized from the nitrogen adsorption-desorption data

3. Results and discussion

3.1 Morphology and structure analyses

KOH activated carbon reaction was a well-known method to form a porous structure in carbon.^[28,29] The morphology and structure of as-prepared CCAC samples (Fig. 1 and Fig. 2). Figs. 1a and b SEM reveal that CCAC-900-4 has abundant micro-/mesopore structure and pore channels of corncob itself. As shown in Fig. 2, with the increase of activation temperature, the micropores become uniform and abundant. However, with the increase of activation dose, many macropores appear and carbon skeleton collapse appears (Figs. 1c-f), which is not conducive to the adsorption of dyes. According to previous reports, the micropore is favorable for adsorption, mesopore can accelerate the transfer of dye ions.^[30,31]

Fig. 2 SEM images of (a) CCAC-700-3, (b) CCAC-800-3.

Fig. 3 (a) FTIR spectra, (b) XRD patterns, (c) N₂ adsorption-desorption isotherm curves and (d) the pore size distribution curves of the CCAC samples.

Table 1. The specific surface, average pore size, total pore volume and adsorption performance of the prepared samples.

Sample	S _{BET} (m ² g ⁻¹)	Average pore size (nm)	Total pore volume (cm ³ g ⁻¹)	Adsorbent dosage (mg)	Adsorption capacitor for 200 mg L ⁻¹ , 50 mL MB (mg g ⁻¹)
CCAC-900-1	1183.39	2.14	0.63	10	441.58
CCAC-900-2	1331.60	2.28	0.75	10	696.08
CCAC-900-3	1741.41	2.11	0.91	10	808.62
CCAC-900-4	2308.27	2.10	1.21	10	896.88
CCAC-900-5	1931.62	2.09	1.04	10	873.17
CCAC-1000-3	1826.92	2.30	1.37	10	692.94
CCAC-700-3	1664.22	2.11	0.87	10	496.14
CCAC-800-3	1881.43	2.12	1.00	10	561.83

The chemical composition of CCAC-700-3, CCAC-800-3, CCAC-1000-3, CCAC-900-1, CCAC-900-2, CCAC-900-3, CCAC-900-4 and CCAC-900-5 were analyzed using FTIR spectra (Fig. 3a). The CCAC-T-m have a relatively similar chemical composition. They have a broad peak at 570-810 cm⁻¹, which can be attributed to C-H band from the aromatic ring. The two peaks at 1023 and 1575 cm⁻¹ corresponding to the stretching vibration of the C-H and aromatic C=C that is highly conjugated to carbonyl groups, respectively.^[32] Additionally, the unsaturated carbon triplet (R-C≡C-H) exists at 1973-2179 cm⁻¹. Fig. 3b shows the crystallinity of as-prepared CCAC-T-m samples by the XRD test. The CCAC-T-m samples display that two diffraction peaks at 23.8° and

43.2°, which were attributed to (002) and (100) planes of the disordered and no obvious graphitization phenomenon carbon materials.^[33,34,28] The broad diffraction peaks indicate that the CCACs prepared by the carbonization activation process have a greater degree of disorder, providing a large number of adsorption sites, which is beneficial to the adsorption of dyes. Further explored the effect of temperature and the amount of activator on the specific surface area and pore structure of the material on adsorption. The CCACs were tested by N₂ adsorption-desorption method. Figs. 3c and 3d shows the BET surface area and pore sizes distribution of the CCAC-T-m. Meanwhile, the data were displayed in Table 1. The adsorption isotherm of samples is type I and IV with a H1-type

Fig. 4 XPS (a) the full- spectra, (b) C1s spectra, and (c) O1s spectra of CCAC-900-4.

hysteresis loop and a sharp capillary condensation step at around 0.4 P/P₀, implying that these are homogeneous micro-/mesoporous structure.^[25,35] From Table 1 can be obtained that the BET surface area fluctuates slightly with increasing temperature, but there is no obvious correlation. Whereas, when the CC: KOH activator from 1:1 increases to 1:5, the specific surface area first increases and then decreases. This phenomenon is due to the increase of the activator dose to enhance the etching of the carbon, which increases the macropores of the carbon material and the three-dimensional structure collapses. Compared with the specific surface area of CCAC-T-m, the CCAC-900-4 has a larger BET surface area (2308.27 m² g⁻¹) and suitable pore size (2.11 nm), which is conducive to the adsorption and transmission of dye molecules. Fig. 4a, the full X-ray photoelectron spectroscopy (XPS) spectra of the CCAC-900-4, where C and O elements were present. In Fig. 4b, the C1s spectra were fitted into three peaks at 284.6, 285.7 and 288.7 eV were C=C, C-O and C=O-C bond, respectively.^[25] Similarly, the high resolution XPS image of O1s existing three peaks 532.3, 533.2 and 533.6 eV (Fig. 4c), which were corresponding to the C-O, C-O-C, O=C-O bond.^[36,37] The results are consistent with the FTIR data.

3.2. Dye and adsorbent selection

Fig. 5 (a) Adsorption capacities and removal efficiency of MB, RhB, NR, CV, MO and CR, (b) comparison of adsorption capacity and removal rate of MB in different CCAC samples.

The actual sewage contains many kinds of dyes. To better explore the adsorption performance of the adsorbent for dyes, using 20 mg CCAC-900-3 to adsorb 200 mg L⁻¹, 50 mL six dyes (MB, RhB, NR, CV, MO, CR) to select the most appropriate dye (Fig. 5a). The adsorption capacity and removal rate of CCAC-900-3 for the six dyes were MB (537.87 mg g⁻¹, 99.67%), RhB (490.84 mg g⁻¹, 99.82%), NR (497.64 mg g⁻¹, 98.04%), CV (397.22 mg g⁻¹, 85.29%), MO (485.19 mg g⁻¹, 96.09%) and CR (391.13 mg g⁻¹, 90.74%), respectively. According to these adsorption capacities and removal rates, MB was selected as the dye adsorption model for CCAC-T-m samples in the next experiment. In Fig. 5b, 10 mg CCAC-T-m adsorb 200 mg L⁻¹, 50 mL MB solution, the adsorption results show an increase first and then decrease with the increase of the temperature and activator, which was consistent with the specific surface area and pore size results of activated carbon materials. The adsorption capacities and removal rate of CCAC-900-1 (441.58 mg g⁻¹, 40.91%), CCAC-900-2 (696.08 mg g⁻¹, 64.49%), CCAC-900-3 (808.62 mg g⁻¹, 74.92%), CCAC-900-4 (896.88 mg g⁻¹, 83.09%), CCAC-900-5 (873.17 mg g⁻¹, 80.90%), CCAC-700-3 (496.14 mg g⁻¹, 45.96%), CCAC-800-3 (561.83 mg g⁻¹, 50.12%) and CCAC-1000-3 (692.94 mg g⁻¹, 64.20%) were display in Table 1 and Fig. 5b. The adsorption results demonstrated that with

Fig. 6 Effect of (a) adsorbent dosage, (b) the MB concentration, (c) pH of MB solution and (d) temperature on adsorption.

the increase of activation ratio and temperature, the adsorption performance showed a trend of increasing first and then decreasing. Among them, CCAC-900-4 has the best adsorption performance for MB. Thus, CCAC-900-4 was selected as the adsorbent for the subsequent study of adsorption conditions and mechanism analysis.

3.3 Effect of adsorbent dosage, the concentration, pH and temperature on adsorption

Further exploration of adsorbent dosage, initial concentration of MB solution, MB solution pH and temperature. First, 5–40 mg CCAC-900-4 was added to 200 mg L⁻¹, 50 mL MB solution with pH = 5.4 at room temperature for adsorption. As shown in Fig. 6a, with the increase of the amount of adsorbent, the amount of adsorption shows a downward trend, while the removal rate increased. When the amount of adsorbent is more than 15 mg, the increase in removal rate tends to be stable. This phenomenon is consistent with previous reports.^[38,39] The result owing to the increase in the dosage of CCAC-900-4 leads to a decrease in the amount of adsorption per unit mass of MB. Additionally, which increases the chance of contact between CCAC-900-4, leads to reducing the number of adsorption sites, thereby hindering CCAC-900-4 adsorption to MB. However, when the dosage of CCAC-900-4 is 15 mg, the optimal adsorption capacity and removal rate of MB to obtain. Therefore, 15 mg CCAC-900 is used as the best dosage for subsequent experiments.

Fig. 6b displays the adsorption experiment results of 15 mg CCAC-900-4 to adsorb different concentrations of MB solution (10–250 mg L⁻¹). With the increase of the

concentration of MB solution, the adsorption capacity was positively correlated with the concentration, while the dye removal rate showed a trend of first increasing and then decreasing. This result can be attributed to the initial concentration of MB solution increase, the contact opportunities of CCAC-900-4 adsorption sites increased. However, with the saturation of adsorption sites, the adsorption capacity gradually decreased. At a low concentration, the adsorption sites were difficult to saturate, so the removal rate is high, while at a high concentration, the adsorption sites were quickly occupied, resulting in a decrease in the removal rate.^[40] The comparison of the adsorption results at different initial concentrations shown that when the initial concentration was 150 mg L⁻¹, the adsorption capacity (519.58 mg g⁻¹) and removal rate (99.6%) were the best, so this concentration was selected as the best concentration for the following experiment.

The pH is a significant factor affecting adsorption performance.^[41] Therefore, 15 mg CCAC-900-4 adsorption 150 mg L⁻¹, 50 mL MB solution at 298 K, pH range in 2–12 was explored. As illustrated in Fig. 6c, when the CCAC-900-4 used to adsorb pH of MB solution is 2–5, the adsorption capacity increases from 502.08 to 523.18 mg g⁻¹, and when the pH increases from 5 to 12, the adsorption capacity decreases from 523.18 to 486.39 mg g⁻¹. However, when the pH < 5, electrostatic interaction occurs between positively charged MB solution and negatively charged CCAC-900-4, which is conducive to adsorption. However, pH > 5, as the pH of the solution increases, the electrostatic interaction between CCAC-900-4 and the solution is weakened, and a large

Fig. 7 (a) Adsorption kinetics, (b) pseudo-first-order kinetic plots, (c) pseudo-second-order kinetic plots and (d-f) multilinear plots of intra-particle diffusion process of MB onto CCAC.

Table 2. Adsorption kinetic equations and parameters of MB by CCAC-900-4.

Kinetic models	Linear equations	Parameters	C_0 (mg L ⁻¹)		
			120	150	180
Pseudo first order	$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$	q_e (mg g ⁻¹)	391.41	438.30	737.46
		k_1 (min ⁻¹)	0.0235	0.0152	0.0177
		R^2	0.9724	0.9780	0.7916
Pseudo second order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	q_e (mg g ⁻¹)	425.53	534.76	684.93
		k_2 (g mg ⁻¹ min ⁻¹)	0.00014	0.00006	0.00005
		R^2	0.9992	0.9974	0.9953
Weber's intraparticle diffusion	$q_t = k_i t^{1/2} + c$	k_{i1} (mg g ⁻¹ min ^{1/2})	60.46	63.51	102.34
		c_1	3.49	3.59	8.81
		R^2	0.9769	0.9779	0.9494
		k_{i2} (mg g ⁻¹ min ^{1/2})	24.95	25.82	24.85
		c_2	110.37	120.00	232.66
		R^2	0.95574	0.9801	0.9939
		k_{i3} (mg g ⁻¹ min ^{1/2})	0.54	3.45	7.78
		c_3	395.63	430.48	492.54
		R^3	0.5276	0.8094	0.8814

amount of OH⁻ combines with MB to occupy many adsorption sites, resulting in a weakened adsorption. Thus, when pH=5, the adsorption capacity and removal rate of CCAC could reach 523.18 mg g⁻¹ and 99.52%, respectively; indicating that CCAC adsorption of MB was suitable for weak acid conditions.

Under the above optimal conditions of the adsorption reaction, the influence of temperature (293~313 K) on the adsorption performance was investigated (Fig. 6d). The adsorption capacity increases with the increase of adsorption

reaction temperature, indicating that the adsorption process is an endothermic reaction. The increase of temperature makes the equilibrium constant increase, which is beneficial to the adsorption reaction.

3.4 Kinetic studies

Fig. 7a shows the adsorption capacity of 15 mg CCAC at the temperature of 25 °C, pH = 5 for the initial concentration of 120, 150 and 180 mg L⁻¹ MB. In the initial stage of adsorption, the adsorption capacity increases rapidly. As time goes by, the

adsorption sites are gradually occupied, and the adsorption capacity increases slowly. When the adsorption time reaches to 360 min, the adsorption reached to adsorption equilibrium, and the adsorption capacities at initial concentrations of 120, 150 and 180 mg L⁻¹ MB were 405.88, 497.45, and 642.21 mg g⁻¹.

To better study the kinetics, the experimental data is fitted by pseudo-first-order dynamics, pseudo-second-order dynamics (Figs. 7b and c) and Table 2 the concentration of MB solution increased from 120 to 180 mg L⁻¹, the q_e , k_1 and k_2 changed randomly.^[38,42] The value of R^2 for pseudo-first-order model was ≤ 0.9780 and pseudo-second-order model was ≥ 0.9953 . Therefore, the adsorption process of CCAC on MB is more in line with the pseudo-secondary model. Since the pseudo-second-order kinetic model assumes that the rate control step may be chemical adsorption, the adsorption process is mainly chemical adsorption.

Figs. 7d-f and Table 2 display that the Weber intraparticle diffusion model was used to study the adsorption process of 120, 150 and 180 mg L⁻¹ MB by CCAC-900-4. The adsorption process is divided into three stages. The first stage is the membrane adsorption process, where MB molecules enter the surface of CCAC from the solution. The second stage corresponds to the diffusion in the pores or particles, and the third part belongs to the final equilibrium stage. The $k_{i1} > k_{i2}$, indicating that this stage is a gradual process. The data graph does not pass through the origin, indicating that intraparticle diffusion is not a rate limiting step. The intercept can reflect the boundary layer effect. The larger intercept indicates that

surface adsorption plays a dominant role in the rate control process. In addition, the values of R_1^2 , R_2^2 and R_3^2 implying that the adsorption process follows the Weber intraparticle diffusion model.

3.5 Adsorption-isotherm

The adsorption isotherm not only provides information on the surface properties and adsorption behavior of the adsorbent, but also helps to study the adsorption mechanism.^[43] As shown in Fig. 8a, when the concentration of MB solution increases from 10 to 250 mg L⁻¹, the adsorption capacities at 293, 298 and 303 K increased from 34.90, 35.38, and 40.35 mg g⁻¹ to 891.57, 982.79, and 989.58 mg g⁻¹, respectively. Simultaneously, the Langmuir adsorption isotherm and Freundlich adsorption isotherm models were used to assess the adsorption performance. The fitting curves and calculating data were seen in Figs. 8b, c and Table 3. The Langmuir adsorption isotherm model assumes that the adsorption is single layer adsorption on the surface of a homogeneous adsorbent, and there is no interaction between the adsorbents.^[44] The q_{max} was 864.58 mg g⁻¹ at 298 K. Compared with other adsorption materials, CCAC has larger adsorption capacity and excellent adsorption performance (Table 4). However, the R^2 value is 0.9417, indicating that the adsorption process is single layer adsorption on the surface of the adsorbent. Additionally, the Freundlich adsorption isotherm is an empirical model assuming that the surface of the adsorbent is not uniform and there is an interaction between the adsorbents.^[42] This R^2 value (0.7372) of the Freundlich model

Fig. 8 (a) adsorption isotherms, (b) Langmuir plot and (c) Freundlich plot for NB adsorption onto CCAC-900-4.

Table 3. Adsorption isotherm equations and parameters of MB by CCAC-900-4.

Isotherm	Equations		T/K		
			293	298	303
Langmuir	$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e}$	q_{max} (mg g ⁻¹)	839.90	864.58	848.59
		K_L (L mg ⁻¹)	0.1799	0.1789	0.1661
		R^2	0.8245	0.9417	0.9524
Freundlich	$q_e = K_F C_e^{\frac{1}{n}}$	K_F (L g ⁻¹)	293.31	348.86	371.70
		n	1.535	1.544	1.389
		R^2	0.6667	0.7372	0.6400

Table 4. Comparison of the adsorption capacity of dyes by various adsorbents.

Adsorbent	Dye	q_m (mg g ⁻¹)	References
ACHC-KOH 1 M	MB	357.38	[45]
HPNC	MB	310.34	[46]
CS	MG	326.93	[47]
HPCs	MB	100	[48]
C _{CH-TS}	MB	604.10	[49]
Al-PILC	MB	474.9	[50]
CCAC-900-4	MB	864.58	This work

fitting curve is lower than Langmuir at 298 K, suggesting that the adsorption process conforms to Langmuir adsorption isotherm, which is a monolayer layer adsorption reaction.

3.6 Adsorption-thermodynamics

Adsorption thermodynamics reveals the effect of temperature on MB adsorption.^[51] Table 5 shows the adsorption thermodynamic equation and the values of thermodynamic parameters (ΔG , ΔS and ΔH). According to the adsorption capacity data of CCAC-900-4 to MB at different temperatures, the adsorption process is an endothermic reaction. The ΔG were -16.36, -16.75 and -17.12 kJ mol⁻¹ at 293, 298 and 303 K, respectively;

which indicating that the adsorption of MB on CCAC-900-4 was spontaneous. The $\Delta H = 6.76$ kJ mol⁻¹ > 0 and $\Delta S = 78.90$ kJ mol⁻¹ > 0 suggesting that the adsorption reaction was irreversible and endothermic reaction. When the $|\Delta H| < 40$ kJ mol⁻¹, the physical adsorption plays a major role. The values of ΔG , ΔS and ΔH confirm that the adsorption reaction of CCAC to MB is an irreversible and spontaneous endothermic reaction. Therefore, increasing the temperature is beneficial to activate more dye molecules, increase the equilibrium constant of the adsorption reaction, and increase the adsorption capacity.

Table 5. Applied thermodynamics equations and parameters of CCAC adsorption MB.

Equation	ΔH (kJ/mol)	ΔS (J/mol/K)	Parameters		
			ΔG /(kJ/mol)		
			293K	298K	303K
$K_d = \frac{q_e}{C_e}$					
$\ln K_d = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$	6.76	78.90	-16.36	-16.75	-17.12
$\Delta G = \Delta H - T\Delta S$

Fig. 9 (a) Cyclic test, (b) optical image of CCAC-900-4 for the adsorption of MB and (c) CAC-900-4 adsorbs simulated sewage.

3.7. Adsorption mechanism of MB by CCAC

Based on the above in-depth research and analysis. In this research, CCAC with negative charge reacts with cationic dye MB through electrostatic interaction and π - π conjugate reaction. When the pH value is lower than 5, the H^+ in the MB solution is more likely to be adsorbed on the surface of the CCAC through electrostatic interaction. When the pH is higher than 5, the OH^- in the MB solution increases, which is not conducive to the occurrence of electrostatic interaction. This is the reaction between the six-ring carbon structure and MB through π - π conjugation. In addition, the large specific surface area and abundant pore structure of CCAC indicate that it is more conducive to physical adsorption.

3.8 Regenerative experiment

Regeneration performance is an important index to evaluate the performance of adsorbents. Here, CCAC-900-4 is recycled by centrifugation, washed with 5 mL of ethanol several times, dried in an oven at 120 °C, then used for MB adsorption again. As shown in Figs. 9a and b, the MB removal rate obtained in the five cycles were 99.67%, 99.55%, 99.52%, 99.42% and 99.34%, respectively. The five cycles test performance almost consistently indicated that CCAC-900-4 has outstanding reproducibility and long-term stability.

3.9 CCAC adsorption experiment for simulated sewage

To further evaluate the ability of CCAC-900-4 to purify actual sewage. The three types of water (tap water, Majiagou and Songhua River water from Harbin, Heilongjiang) were selected from nature to simulate actual sewage. Here, at room temperature, 15 mg CCAC-900-4 was used to adsorb 150 mg L^{-1} , 50 mL MB prepared from three kinds of natural water. As illustrated in Fig. 9c, the adsorption capacity and removal rate of CCAC-900-4 for the three types of water were tap water (607.12 mg g^{-1} , 99.68%), Majiagou (591.95 mg g^{-1} , 99.68%) and Songhua River (595.91 mg g^{-1} , 99.71%), respectively; which indicated that CCAC-900-4 can almost completely remove 150 mg L^{-1} , 50 mL MB. This excellent result shows that CCAC-900-4 has excellent purification ability for actual sewage.

4. Conclusions

In this work, CCAC with the large specific surface and porous structure was successfully prepared by a simple KOH activation method. The CCAC samples with different temperatures and different activation ratios were compared, and the adsorption process of MB on CCAC-900-4 was comprehensively studied. The results show that the adsorption capacity of CCAC-900-4 to MB is 523.18 mg g^{-1} . The process conforms to Langmuir and pseudo-second-order kinetic models, while the adsorption reaction is a spontaneous endothermic reaction. More importantly, CCAC-900-4 has excellent reproducibility. After five cycles of tests, the removal rate of MB is still 99.32%. This work provides a pathway for the subsequent utilization of biomass waste and

the removal of environmental pollutants.

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Conflict of interest

There are no conflicts to declare.

Supporting information

Not applicable.

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