

Nonadditive interactions during co-pyrolysis of sewage sludge and corn straw and their implications for KOH activation and methylene blue adsorption

Feng Peng

Chongqing University of Science and Technology

Shunhong Lin

1993025@cqust.edu.cn

Chongqing University of Science and Technology

Luyu Wang

Chongqing University of Science and Technology

Research Article

Keywords: Sewage sludge, Corn straw, Co-pyrolysis, KOH activation, Methylene blue

Posted Date: September 29th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10995856/v1>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: No competing interests reported.

Abstract

Porous carbons were prepared from sewage sludge (SS) and corn straw (CS) by co-pyrolysis and KOH activation to examine the relationship between precursor thermal behavior and adsorption performance. Individual feedstocks were analyzed thermogravimetrically at $10\text{--}30^\circ\text{C min}^{-1}$, and blends were compared at $10^\circ\text{C min}^{-1}$. Deviations between measured and mass-weighted theoretical thermogravimetric curves revealed stage-dependent nonadditive interactions. At $10^\circ\text{C min}^{-1}$, the maximum mass-loss rates of CS and SS were 7.19 and $1.80\% \text{ min}^{-1}$, at 345.95 and 291.99°C , respectively. The 1:1 SS:CS blend balanced pyrolytic reactivity and solid retention and was selected as the activated-carbon precursor. Following precarbonization at 550°C , KOH activation was optimized using an $L16(4^4)$ orthogonal design. The selected conditions were SS:CS = 1:1, an impregnation ratio of 1:3, an activation temperature of 800°C and an activation time of 90 min. The iodine number reached 945.50 mg g^{-1} , with a mean of $945.24 \pm 21.37 \text{ mg g}^{-1}$ in three validation experiments. Activation increased the BET specific surface area from 79.88 to $647.69 \text{ m}^2 \text{ g}^{-1}$ and total pore volume from 0.1198 to $0.445 \text{ cm}^3 \text{ g}^{-1}$. The resulting carbon, KSC800, had a Langmuir maximum methylene blue adsorption capacity of 110.38 mg g^{-1} . After five regeneration cycles, its adsorption capacity was 64.65 mg g^{-1} , corresponding to 69.44% retention. These results link thermogravimetric precursor selection to the development of a microporous–mesoporous carbon with effective dye adsorption and regeneration performance.

1 Introduction

The expansion of wastewater treatment has increased sewage sludge production. Its high moisture content, inorganic minerals, organic contaminants and potentially mobile heavy metals complicate treatment and resource recovery. Pyrolysis can reduce sludge volume, stabilize some organic constituents and convert the solid residue into a carbonaceous material. However, sludge-derived chars typically have high ash contents and poorly developed pore structures, limiting their direct use as adsorbents [1, 2]. Both precursor composition and activation conditions therefore influence the properties of the final material.

Corn straw provides an additional carbon source for sludge. Compared with sludge, straw has a higher volatile matter content and a lower ash content, and its lignocellulosic constituents decompose within characteristic temperature ranges. In blends, sludge favors solid retention, whereas straw promotes volatile release and the formation of initial pore channels. Studies of sludge co-pyrolysis with sawdust, cotton stalks and coconut shells have shown that feedstock interactions modify mass-loss behavior and char properties [3–5]. Thermal behavior, activation conditions and adsorption performance have often been examined separately; the relationship between precursor selection and final material performance warrants further investigation.

The thermogravimetric (TG) curve of a blend often deviates from the mass-weighted sum of the individual feedstock curves. Such deviations are associated with heat and mass transfer, reactions among volatile products, and catalytic or inhibitory effects of mineral constituents [3, 4]. Here, the

difference between measured and theoretical TG curves was used to characterize nonadditive interactions and compare pyrolysis behavior across blending ratios.

Chemical activation further develops the pore structure of char precursors. Among alkaline activating agents, KOH promotes pore formation through carbon consumption, expansion between carbon layers and pore development [6, 8]. The resulting structure depends on feedstock composition, activating-agent dosage, activation temperature and residence time. Excessive activation may widen micropores or damage the carbon framework, whereas insufficient activation limits pore development [5, 6, 9]. Studies of sludge-derived adsorbents also show that the activation method and agent affect pore structure, material yield and contaminant adsorption [20–23]. These factors should therefore be considered together when selecting precursors and optimizing activation conditions.

The cationic dye methylene blue (MB) was selected to evaluate pore accessibility and surface affinity. MB is widely used as a probe contaminant in studies of sludge- and biomass-derived activated carbons [13–15, 20, 22, 24]. Equilibrium, kinetic and regeneration experiments were used to compare three activated carbons, and the adsorption mechanisms were interpreted by combining model fits with pore structure and surface characterization [16–19].

This study first compares the pyrolysis behavior of sewage sludge and corn straw and examines nonadditive interactions at different blending ratios using deviations between measured and theoretical TG curves. A char precursor is then selected, two-step KOH activation is optimized, and changes in pore structure and surface properties are characterized. Finally, MB adsorption and regeneration experiments are used to evaluate material performance.

2 Materials and methods

2.1 Feedstocks and basic properties

Dewatered sewage sludge was collected from a wastewater treatment plant in Chongqing, China, and corn straw was obtained from a rural area of Chongqing. During initial pretreatment, the feedstocks were dried at 105°C for 48 h, ground, passed through a 100-mesh sieve and stored in sealed containers. Before each experiment, they were dried again at 105°C for 12 h. Sewage sludge and corn straw are denoted SS and CS, respectively. All blending ratios are expressed as dry-mass ratios of SS:CS.

Analytical-grade KOH, NaOH, KI, KIO₃, I₂, soluble starch, Na₂S₂O₃ and HCl were purchased from Chengdu Kelong Chemical Co., Ltd., China. Analytical-grade methylene blue was purchased from Tianjin Zhiyuan Chemical Reagent Co., Ltd., China.

Table 1
Proximate and ultimate analyses of the feedstocks on a dry basis

Sample	V _d / %	A _d / %	FC _d / %	C _d / %	H _d / %	O _d / %	N _d / %	S _d / %
SS	48.02	47.92	4.06	25.61	3.58	17.57	4.43	0.89
CS	74.35	7.31	18.34	34.15	3.47	53.01	1.70	0.36

V_d, volatile matter; A_d, ash; FC_d, fixed carbon. O_d was calculated by difference.

2.2 Thermogravimetric analysis and interaction deviations

TG measurements were performed using a NETZSCH STA 409 PC simultaneous thermal analyzer. Approximately 10 mg of sample was placed in a covered Al₂O₃ crucible and heated under N₂ of 99.999% purity. Individual SS and CS samples were tested at 10, 20 and 30°C min⁻¹. The N₂ flow rate was 50 mL min⁻¹ for all three SS measurements and 50, 30 and 50 mL min⁻¹ for the CS measurements at 10, 20 and 30°C min⁻¹, respectively. Blends with SS:CS dry-mass ratios of 1:1, 2:1, 3:1 and 4:1 were tested at 10°C min⁻¹ under N₂ flowing at 50 mL min⁻¹. All curves used for direct comparisons were normalized to the initial sample mass and analyzed over a common temperature interval of 30–800°C. TG curves and characteristic parameters were interpreted following approaches commonly used in studies of the thermal conversion of sludge and lignocellulosic constituents [10, 11].

The theoretical residual-mass curve of each blend was calculated from the independently measured curves of the individual feedstocks, weighted by their mass fractions:

$$W_{\text{cal}}(T) = x_{\text{SS}}W_{\text{SS}}(T) + x_{\text{CS}}W_{\text{CS}}(T)$$

where W_{cal} is the theoretical residual mass, W_{SS} and W_{CS} are the residual masses of SS and CS at the same temperature, and x_{SS} and x_{CS} are their dry-mass fractions. The interaction deviation was defined as:

$$\Delta W(T) = W_{\text{exp}}(T) - W_{\text{cal}}(T)$$

A negative deviation ($\Delta W < 0$) indicates that the measured residual mass is lower than the theoretical value, corresponding to enhanced mass loss. A positive deviation ($\Delta W > 0$) indicates a higher measured residual mass, corresponding to inhibited mass loss or enhanced solid retention.

2.3 Precarbonization and chemical activation

The selected SS–CS blend was placed in a crucible and heated to 550°C at 10°C min⁻¹ in an OTF-1100X horizontal tube furnace under N₂ flowing at 200 mL min⁻¹. Heating was stopped when the target temperature was reached, and the sample was allowed to cool inside the furnace under N₂. The resulting unactivated sludge–straw char is denoted RSC.

For chemical impregnation, RSC was mixed with the corresponding activating-agent solution and shaken at 25°C and 220 rpm for 24 h, after which the solid was recovered by filtration. The impregnated sample was heated to the specified activation temperature at 10°C min⁻¹ under N₂ flowing at 200 mL min⁻¹. After furnace cooling, the sample was washed with 1 mol L⁻¹ HCl and then with deionized water until the washings reached pH 6–7, followed by drying and grinding. Samples activated at 800°C with KOH, mixed KOH/NaOH and NaOH are denoted KSC800, KNSC800 and NSC800, respectively. For the selected KOH activation conditions, the impregnation ratio is defined as the mass of RSC to the volume of KOH solution: 1:3 represents 1 g of RSC mixed with 3 mL of 3 mol L⁻¹ KOH solution. For mixed-alkali activation, KOH and NaOH solutions, each at 3 mol L⁻¹, were combined at a KOH:NaOH ratio of 1.5:1.5.

2.4 Process optimization and iodine number determination

Single-factor experiments examined the effects of SS:CS ratio, impregnation ratio, activation temperature and activation time and were used to establish four levels for each factor. KOH activation gave the highest iodine number among the three activation systems and was therefore selected for the L16(4⁴) orthogonal experiment. The iodine number was determined according to GB/T 12496.8–2015 [12]. Range analysis was used to assess factor effects. The selected combination was validated in three experiments. All other results represent single measurements.

Table 2
Factors and levels in the L16 orthogonal design

Level	A: SS:CS	B: Impregnation ratio	C: Activation temperature / °C	D: Activation time / min
1	1:1	1:1	600	30
2	2:1	1:2	700	60
3	3:1	1:3	800	90
4	4:1	1:4	900	120

2.5 Material characterization

Surface morphology was examined using an Apreo 2 C HiVac field-emission scanning electron microscope at an accelerating voltage of 10 kV, and elemental distributions were determined by energy-dispersive X-ray spectroscopy (EDS). N₂ adsorption–desorption measurements were performed using a BELSORP-max surface area and pore size analyzer after vacuum degassing at 300°C for 20 h. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method, and total pore volume and pore size distributions were obtained from the adsorption data. Micropore and mesopore distributions were evaluated using the Horváth–Kawazoe and Barrett–Joyner–Halenda (BJH) methods, respectively. Crystalline phases were analyzed using a SmartLab X-ray diffractometer with Cu Kα₁ radiation (λ = 1.540593 Å), operated at 40 kV and 100 mA. The 2θ range was 10–90°, with a step size of 0.02° and a scan rate of 10° min⁻¹. Surface functional groups were analyzed using a Bruker TENSOR 27 Fourier transform infrared (FTIR) spectrometer over 4000–500 cm⁻¹.

2.6 Methylene blue adsorption and regeneration

An MB stock solution of 1000 mg L⁻¹ was prepared and stored at 4°C in the dark. Standard solutions of 2–10 mg L⁻¹ were prepared, and absorbance was measured at 665 nm using an N4 UV–visible spectrophotometer. Batch adsorption experiments were conducted at room temperature in a SHA-C thermostatic water-bath shaker to examine the effects of contact time (30–180 min), initial MB concentration (20–120 mg L⁻¹), adsorbent dosage (0.10–0.35 g) and initial pH (1–11). Unless a parameter was being varied, the conditions were 0.10 g of adsorbent, 100 mL of 100 mg L⁻¹ MB solution and a contact time of 150 min. Adsorption isotherm experiments used 0.10 g of adsorbent and 100 mL of solution with an equilibration time of 180 min.

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100\%$$

$$q_e = \frac{(C_0 - C_e)V}{m}$$

where C_0 and C_e are the initial and equilibrium MB concentrations (mg L⁻¹), respectively, V is the solution volume (L), m is the adsorbent mass (g), and q_e is the equilibrium adsorption capacity (mg g⁻¹).

Equilibrium data were fitted using the linearized Langmuir and Freundlich models. Time-dependent data were fitted using the pseudo-first-order, pseudo-second-order and Weber–Morris intraparticle diffusion models [18, 19].

For regeneration, KSC800 was recovered after MB adsorption at $C_0 = 100$ mg L⁻¹, $m = 0.10$ g and $t = 150$ min, added to 50 mL of 1 mol L⁻¹ HCl and shaken at 200 rpm for 4 h in the dark. The solid was then separated, washed to neutral pH and dried at 100°C to constant mass before reuse. Five adsorption–desorption cycles were performed.

3 Results and discussion

3.1 Complementary thermal behavior and nonadditive interactions during co-pyrolysis

The feedstocks differed substantially in composition (Table 1). SS contained 47.92% ash and 4.06% fixed carbon, whereas CS contained 7.31% ash, 18.34% fixed carbon and 74.35% volatile matter. The mineral fraction of SS favors solid retention but reduces the proportion of organic constituents. The more reactive lignocellulosic components of CS release volatile products during carbonization and form initial mass-transfer channels. The two feedstocks therefore offer complementary characteristics in terms of solid retention and volatile release.

At 10°C min⁻¹, the main derivative thermogravimetric (DTG) peak of CS occurred at 345.95°C, with a maximum mass-loss rate of 7.19% min⁻¹. SS decomposed over a broader temperature range and showed a less intense peak at 291.99°C, with a maximum mass-loss rate of 1.80% min⁻¹. The residual

solid fractions at 800°C were 20.84% for CS and 54.40% for SS. Increasing the heating rate shifted the characteristic temperatures of both individual feedstocks toward higher temperatures and increased the absolute DTG peak magnitudes, consistent with greater thermal lag [10, 11]. The CS measurement at 20°C min⁻¹ used a different N₂ flow rate, so its comparison with the other heating rates also includes a gas-flow difference. The main text focuses on 10°C min⁻¹ to match the blend experiments.

Table 3
Pyrolysis characteristics of the samples at 10°C min⁻¹

Sample	T _i / °C	T _{max} / °C	T _f / °C	Maximum mass-loss rate / % min ⁻¹	Residual solid at 800°C / %
SS	189.04	291.99	534.81	1.80	54.40
CS	184.07	345.95	568.18	7.19	20.84
1SS:1CS	188.33	348.79	400.62	3.81	39.41
2SS:1CS	180.52	327.49	392.10	2.87	41.78
3SS:1CS	179.10	321.10	395.65	2.66	47.59
4SS:1CS	175.55	318.97	404.17	2.28	48.97

T_i, onset decomposition temperature; T_{max}, DTG peak temperature; T_f, temperature at which mass loss reaches 95% of the combustible fraction of the sample. Blend residual-solid values at approximately 800°C correspond to the recorded temperature of 799.64°C.

As the SS fraction increased, T_{max} decreased from 348.79°C for 1SS:1CS to 318.97°C for 4SS:1CS, and the maximum mass-loss rate decreased from 3.81 to 2.28% min⁻¹. The 1:1 blend retained 39.41% solid at 800°C, exceeding the value for CS, while its pyrolytic reactivity was appreciably higher than that of SS. This ratio provided a balance between solid retention and volatile release and was selected for subsequent carbon preparation.

The deviation between measured and theoretical TG curves varied with temperature and blending ratio (Fig. 1). During the main devolatilization stage, ΔW was negative for all four blends, indicating enhanced mass loss. The 1:1 and 4:1 curves became positive at approximately 348°C, whereas the 3:1 curve became positive at approximately 418°C and remained positive at higher temperatures. For the 2:1 blend, ΔW was positive at approximately 366–562°C and then became negative again, reaching – 1.43% at 800°C. Thus, the blending ratio altered both the temperature interval and direction of the nonadditive interaction. Negative deviations may reflect catalysis of straw decomposition by sludge minerals, including alkali and alkaline-earth metals. Positive deviations may be associated with mineral stabilization, secondary condensation of volatile products or char-forming reactions [3, 4].

3.2 Optimization of precarbonization and KOH activation

Increasing the precarbonization temperature from 450 to 750°C decreased the sludge-char yield from 63.22 to 55.35% and increased the ash content from 73.21 to 83.14%. The iodine number increased from 195.4 mg g⁻¹ at 450°C to 271.6 mg g⁻¹ at 550°C and then decreased at higher temperatures. A precarbonization temperature of 550°C was therefore selected to retain a reactive carbon framework while limiting ash enrichment and high-temperature densification. Similar temperature dependence has been reported for sludge pyrolysis and sludge-derived carbon preparation [7, 10].

Table 4
Effect of precarbonization temperature on sludge-char properties

Precarbonization temperature / °C	Char yield / %	Ash / %	pH	Iodine number / mg g ⁻¹
450	63.22	73.21	8.59	195.4
550	58.62	77.57	9.61	271.6
650	56.93	81.56	10.63	263.2
750	55.35	83.14	11.17	224.8

The single-factor experiments identified relatively high iodine numbers at SS:CS = 1:1, an impregnation ratio of 1:3, an activation temperature of 800°C and an activation time of 90 min. Among the three activation systems, KOH gave the highest iodine number and was selected for the subsequent orthogonal experiment. This finding is consistent with reports that potassium-containing species promote carbon-framework etching and pore formation [6, 8, 9].

Table 5
Range analysis of the L16 orthogonal experiment using iodine number (mg g⁻¹) as the response

Statistic	A: SS:CS	B: Impregnation ratio	C: Activation temperature	D: Activation time
Mean at level 1	754.0200	561.3450	530.2275	575.7050
Mean at level 2	682.2175	637.9350	635.5425	671.4450
Mean at level 3	610.4125	704.9550	731.2825	690.5950
Mean at level 4	533.8175	676.2325	683.4150	642.7225
Range R	220.2025	143.6100	201.0550	114.8900

Factor levels are defined in Table 2.

The factor ranges followed the order A > C > B > D, indicating that feedstock ratio and activation temperature produced the largest response variations within the investigated levels. The highest measured iodine number in the L16 experiment, 945.50 mg g⁻¹, was obtained for A1B3C3D3: SS:CS = 1:1,

an impregnation ratio of 1:3, 800°C and 90 min. Three validation experiments gave iodine numbers of 923.16, 965.82 and 946.74 mg g⁻¹, with a mean ± sample standard deviation of 945.24 ± 21.37 mg g⁻¹ and a relative standard deviation of 2.26%. The KOH-activated carbon prepared under these conditions is denoted KSC800.

3.3 Structural evolution induced by KOH activation

SEM images showed a relatively dense RSC surface with large channels associated with the biomass structure. KSC800 exhibited pronounced surface etching, thinner pore walls and numerous openings, indicating restructuring of the carbon framework during KOH activation. EDS mapping revealed a predominantly carbonaceous matrix with unevenly distributed Si, O, S, P and K. Some mineral elements remained after acid washing, producing a carbon–mineral composite. Similar morphological changes and mineral residues have been reported for activated carbons derived from sludge and biomass [5, 7, 8].

The pore structure parameters confirmed the substantial effect of KOH activation (Table 6). The BET specific surface area increased from 79.88 m² g⁻¹ for RSC to 647.69 m² g⁻¹ for KSC800, an approximately 711% increase, while the total pore volume increased from 0.1198 to 0.445 cm³ g⁻¹. The mean pore diameter decreased from 5.99 to 2.75 nm. A distinct micropore contribution developed at approximately 0.6 nm, together with a broad mesopore contribution at approximately 2–10 nm. Narrow micropores provide potential adsorption sites, whereas larger channels facilitate solute transport; their coexistence can support both adsorption capacity and accessibility [5, 9, 16, 20–23].

Table 6 Pore structure parameters before and after KOH activation			
Sample	S _{BET} / m ² g ⁻¹	Total pore volume / cm ³ g ⁻¹	Mean pore diameter / nm
RSC	79.88	0.1198	5.99
KSC800	647.69	0.445	2.75

The XRD pattern of RSC exhibited sharp reflections at 2θ ≈ 20.9°, 26.6° and 50.1°, consistent with quartz (SiO₂; PDF 46-1045). These reflections weakened after KOH activation and acid washing, suggesting partial mineral transformation or removal. KSC800 showed a broad scattering feature over 20–30°, characteristic of a disordered carbon structure. Some additional reflections were tentatively associated with sanidine-type aluminosilicates: disordered sanidine, KAlSi₃O₈ (PDF 25–0618), and sanidine, (K,Na)AlSi₃O₈ (PDF 19-1227). These assignments require further confirmation [7, 9].

The FTIR bands of RSC at approximately 3433, 1626 and 1088 cm⁻¹ were assigned to O–H stretching, aromatic C = C and/or conjugated C = O vibrations, and Si–O–Si stretching, respectively. After activation, the corresponding bands shifted to approximately 3410, 1582 and 1080 cm⁻¹, with changes in intensity, indicating modification of oxygen-containing surface groups and mineral-associated groups [7, 16]. Quantitative analysis is needed to establish changes in functional-group abundance.

3.4 Methylene blue adsorption performance

KSC800 maintained a higher MB removal efficiency than the other two activated carbons throughout the investigated contact-time range. Adsorption was rapid during the first 60 min and approached equilibrium after approximately 150 min, with a maximum removal efficiency of 93.1%. A contact time of 150 min was adopted for the subsequent factor experiments. Rapid initial uptake is consistent with readily accessible sites on external surfaces and connected mesopores. The slower subsequent stage may involve continued solute diffusion into smaller pores [13–15, 17, 20, 22, 24].

As the initial MB concentration increased from 20 to 120 mg L⁻¹, the removal efficiency of KSC800 decreased from 99.9 to 89.6%, while its adsorption capacity increased from 19.98 to 107.52 mg g⁻¹. Removal efficiency measures the fraction of MB removed from solution, whereas adsorption capacity measures the MB loading per unit adsorbent mass, explaining their different concentration-dependent trends. Increasing the adsorbent dosage improved removal efficiency. Removal was also higher under alkaline than strongly acidic conditions, consistent with reduced H⁺ competition and stronger attraction between cationic MB and deprotonated surface groups [16, 17].

The equilibrium fitting results are summarized in Table 7. For KNSC800 and NSC800, the Langmuir R² values were 0.9925 and 0.9971, exceeding the corresponding Freundlich values of 0.9620 and 0.9612 and indicating more pronounced Langmuir-type behavior. For KSC800, the Freundlich R² of 0.9881 was slightly higher than the Langmuir value of 0.9812, consistent with a more heterogeneous distribution of adsorption-site energies. The Langmuir maximum adsorption capacities were 110.38, 103.20 and 92.85 mg g⁻¹ for KSC800, KNSC800 and NSC800, respectively [16–18].

Table 7
Langmuir and Freundlich parameters for MB adsorption

Sample	$q_{\max}$ / mg g ⁻¹	K_L / L mg ⁻¹	Langmuir R ²	K_F	n	Freundlich R ²
KSC800	110.38	1.1137	0.9812	54.01	3.7806	0.9881
KNSC800	103.20	0.2767	0.9925	26.57	2.4439	0.9620
NSC800	92.85	0.1417	0.9971	17.06	2.2373	0.9612

$q_{\max}$ is the calculated maximum monolayer adsorption capacity. K_F is the Freundlich adsorption constant; its dimensions depend on 1/n.

For all three activated carbons, the pseudo-second-order model gave higher R² values than the pseudo-first-order model. For KSC800, the pseudo-second-order R² was 0.9999 and the calculated equilibrium adsorption capacity was 97.56 mg g⁻¹, indicating that this equation described the time-dependent data well [18]. None of the Weber–Morris fitted lines passed through the origin, indicating that intraparticle diffusion was not the sole rate-controlling process and that boundary-layer mass transfer also contributed [19].

Table 8
Kinetic model parameters for MB adsorption

Sample	PFO q_e / mg g ⁻¹	k_1 / min ⁻¹	PFO R ²	PSO q_e / mg g ⁻¹	k_2 / g mg ⁻¹ min ⁻¹	PSO R ²
KSC800	93.1	0.02815	0.9962	97.56	0.00124	0.9999
KNSC800	84.4	0.03226	0.9671	94.52	0.00053	0.9984
NSC800	72.8	0.02935	0.9599	84.96	0.00041	0.9966

PFO, pseudo-first-order model; PSO, pseudo-second-order model.

3.5 Regeneration performance

The equilibrium adsorption capacity of KSC800 decreased with repeated acid-assisted regeneration. Its initial capacity was 93.10 mg g⁻¹ and decreased to 88.45 mg g⁻¹ after the first regeneration, corresponding to 95.01% retention. After the fifth regeneration, the capacity was 64.65 mg g⁻¹, with 69.44% retention. At $C_0 = 100$ mg L⁻¹, $V = 0.10$ L and $m = 0.10$ g, q_e expressed in mg g⁻¹ is numerically equal to removal efficiency expressed as a percentage. The MB removal efficiency after the fifth regeneration was therefore 64.65%.

4 Conclusions

Co-pyrolysis of sewage sludge and corn straw exhibited pronounced stage-dependent nonadditive interactions. All four blends showed enhanced mass loss during the main devolatilization stage, whereas the direction of the interaction at higher temperatures depended on the blending ratio. At 10°C min⁻¹, the 1:1 SS:CS blend had a maximum mass-loss rate of 3.81% min⁻¹ and retained 39.41% solid at 800°C, providing a balance between pyrolytic reactivity and solid retention.

Following precarbonization at 550°C, the selected KOH activation conditions were an impregnation ratio of 1:3, an activation temperature of 800°C and an activation time of 90 min. The iodine number reached 945.50 mg g⁻¹ in the orthogonal experiment and 945.24 ± 21.37 mg g⁻¹ in three validation experiments. KOH activation increased the BET specific surface area from 79.88 to 647.69 m² g⁻¹ and the total pore volume from 0.1198 to 0.445 cm³ g⁻¹, producing a carbon–mineral composite with coexisting micropores and mesopores.

KSC800 exhibited the highest MB adsorption capacity among the three activated carbons. Its Freundlich R² was slightly higher than its Langmuir R², whereas KNSC800 and NSC800 showed more pronounced Langmuir-type behavior. The Langmuir maximum adsorption capacity of KSC800 was 110.38 mg g⁻¹. After the fifth regeneration, its capacity was 64.65 mg g⁻¹, corresponding to 69.44% retention. The co-pyrolysis thermal behavior provides a basis for selecting the feedstock ratio, while the microporous–mesoporous structure developed by KOH activation improves adsorption performance.

Declarations

Funding: No funding was received for this study.

Competing interests: The authors declare no competing interests relevant to this article.

Author contributions: Feng Peng: Investigation, formal analysis, writing – original draft. Shunhong Lin: Conceptualization, methodology, supervision, writing – review and editing. Luyu Wang: Investigation, data curation, writing – review and editing.

Data availability: The data supporting the findings of this study are available from the corresponding author upon reasonable request.

Use of large language models

As non-native English speakers, we used a large language model to assist with English translation and language editing, including improvements to grammar, clarity and idiomatic expression.

References

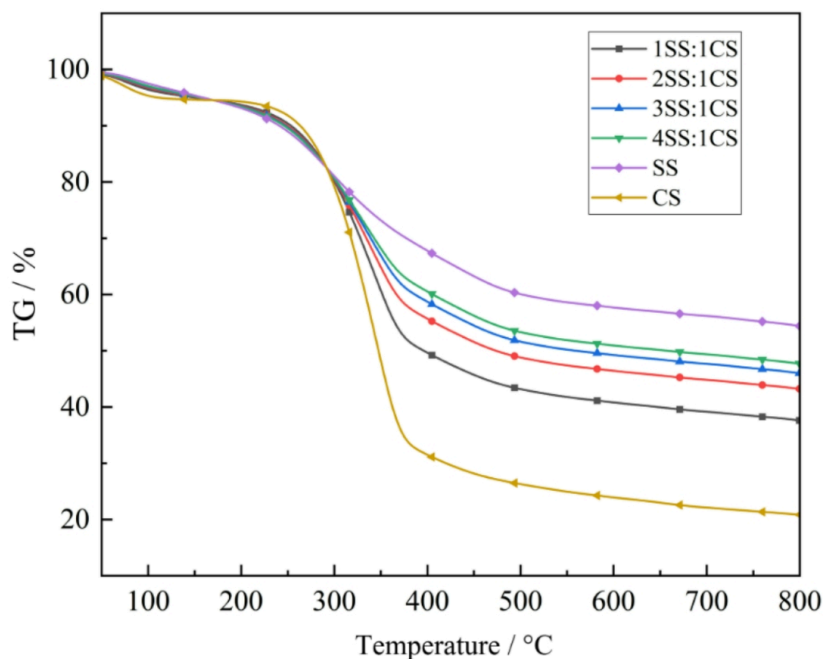
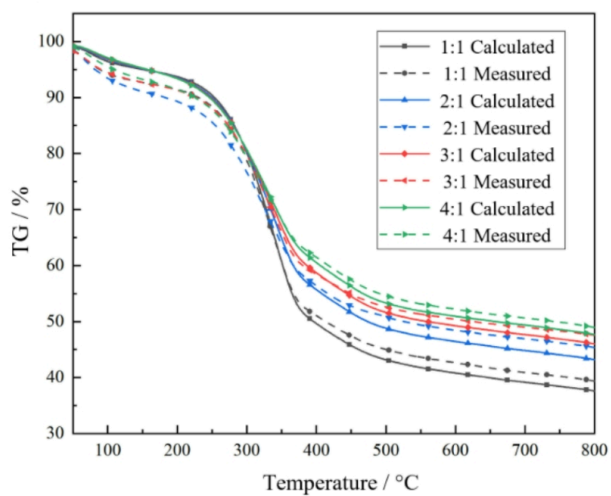
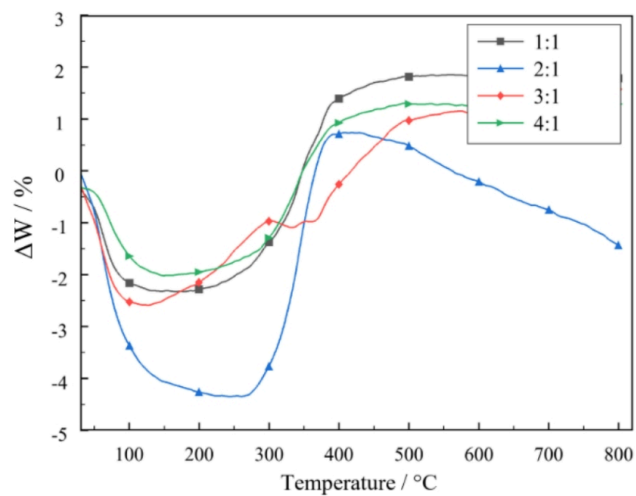
1. Raček J, Ševčík J, Chorazy T, et al. Biochar-recovery material from pyrolysis of sewage sludge: a review. *Waste Biomass Valor.* 2020;11:3677–3709. <https://doi.org/10.1007/s12649-019-00679-w>
2. Zhao L, Sun ZF, Pan XW, et al. Sewage sludge derived biochar for environmental improvement: advances, challenges, and solutions. *Water Res X.* 2023;18:100167. <https://doi.org/10.1016/j.wroa.2023.100167>
3. Huang HJ, Yang T, Lai FY, et al. Co-pyrolysis of sewage sludge and sawdust/rice straw for the production of biochar. *J Anal Appl Pyrolysis.* 2017;125:61–68. <https://doi.org/10.1016/j.jaap.2017.04.018>
4. Wang Z, Xie L, Liu K, et al. Co-pyrolysis of sewage sludge and cotton stalks. *Waste Manag.* 2019;89:430–438. <https://doi.org/10.1016/j.wasman.2019.04.033>
5. Yang B, Liu Y, Liang Q, et al. Evaluation of activated carbon synthesized by one-stage and two-stage co-pyrolysis from sludge and coconut shell. *Ecotoxicol Environ Saf.* 2019;170:722–731. <https://doi.org/10.1016/j.ecoenv.2018.11.130>
6. Gao Y, Yue Q, Gao B, et al. Insight into activated carbon from different kinds of chemical activating agents: a review. *Sci Total Environ.* 2020;746:141094. <https://doi.org/10.1016/j.scitotenv.2020.141094>
7. Li Y, Chang F, Huang B, et al. Activated carbon preparation from pyrolysis char of sewage sludge and its adsorption performance for organic compounds in sewage. *Fuel.* 2020;266:117053. <https://doi.org/10.1016/j.fuel.2020.117053>
8. Fu Y, Shen Y, Zhang Z, et al. Activated biochars derived from rice husk via one- and two-step KOH-catalyzed pyrolysis for phenol adsorption. *Sci Total Environ.* 2019;646:1567–1577.

<https://doi.org/10.1016/j.scitotenv.2018.07.423>

9. Liou TH, Wu SJ. Characteristics of microporous/mesoporous carbons prepared from rice husk under base- and acid-treated conditions. *J Hazard Mater.* 2009;171:693–703.
<https://doi.org/10.1016/j.jhazmat.2009.06.056>
10. Gao N, Li J, Qi B, et al. Thermal analysis and products distribution of dried sewage sludge pyrolysis. *J Anal Appl Pyrolysis.* 2014;105:43–48. <https://doi.org/10.1016/j.jaap.2013.10.002>
11. Chen WH, Kuo PC. Isothermal torrefaction kinetics of hemicellulose, cellulose, lignin and xylan using thermogravimetric analysis. *Energy.* 2011;36:6451–6460.
<https://doi.org/10.1016/j.energy.2011.09.022>
12. GB/T 12496.8–2015. Test methods of wooden activated carbon—Determination of iodine number. Standardization Administration of China, Beijing (2015).
13. Sierra I, Iriarte-Velasco U, Gamero M, et al. Upgrading of sewage sludge by demineralization and physical activation with CO₂: application for methylene blue and phenol removal. *Microporous Mesoporous Mater.* 2017;250:88–99. <https://doi.org/10.1016/j.micromeso.2017.05.020>
14. Jindarom C, Meeyoo V, Kitiyanan B, et al. Surface characterization and dye adsorptive capacities of char obtained from pyrolysis/gasification of sewage sludge. *Chem Eng J.* 2007;133:239–246.
<https://doi.org/10.1016/j.cej.2007.02.002>
15. Wong S, Yac'cob NAN, Ngadi N, et al. From pollutant to solution of wastewater pollution: synthesis of activated carbon from textile sludge for dye adsorption. *Chin J Chem Eng.* 2018;26:870–878.
<https://doi.org/10.1016/j.cjche.2017.07.015>
16. Li L, Quinlivan PA, Knappe DRU. Effects of activated carbon surface chemistry and pore structure on the adsorption of organic contaminants from aqueous solution. *Carbon.* 2002;40:2085–2100.
[https://doi.org/10.1016/s0008-6223\(02\)00069-6](https://doi.org/10.1016/s0008-6223(02)00069-6)
17. Han Q, Wang J, Goodman BA, et al. High adsorption of methylene blue by activated carbon prepared from phosphoric-acid-treated eucalyptus residue. *Powder Technol.* 2020;366:239–248.
<https://doi.org/10.1016/j.powtec.2020.02.013>
18. Wang J, Guo X. Adsorption kinetic models: physical meanings, applications, and solving methods. *J Hazard Mater.* 2020;390:122156. <https://doi.org/10.1016/j.jhazmat.2020.122156>
19. Singh SK, Townsend TG, Mazyck D, et al. Equilibrium and intra-particle diffusion of stabilized landfill leachate onto micro- and meso-porous activated carbon. *Water Res.* 2012;46:491–499.
<https://doi.org/10.1016/j.watres.2011.11.007>
20. Li WH, Yue QY, Gao BY, et al. Preparation and utilization of sludge-based activated carbon for the adsorption of dyes from aqueous solutions. *Chem Eng J.* 2011;171:320–327.
<https://doi.org/10.1016/j.cej.2011.04.012>
21. Méndez A, Gascó G, Freitas MMA, et al. Preparation of carbon-based adsorbents from pyrolysis and air activation of sewage sludges. *Chem Eng J.* 2005;108:169–177.
<https://doi.org/10.1016/j.cej.2005.01.015>

22. Lu J, Zhang Q, An Q, et al. Preparation of activated carbon from sewage sludge using green activator and its performance on dye wastewater treatment. *Environ Technol.* 2023;44:3897–3910.
<https://doi.org/10.1080/09593330.2022.2077130>
23. Zhang L, Pan J, Liu L, et al. Combined physical and chemical activation of sludge-based adsorbent enhances Cr(VI) removal from wastewater. *J Clean Prod.* 2019;238:117904.
<https://doi.org/10.1016/j.jclepro.2019.117904>
24. Kumar A, Jena HM. Removal of methylene blue and phenol onto prepared activated carbon from fox nutshell by chemical activation in batch and fixed-bed column. *J Clean Prod.* 2016;137:1246–1259.
<https://doi.org/10.1016/j.jclepro.2016.07.177>

Figures

(a)**(b)****(c)****Figure 1**

Thermal behavior and nonadditive interactions at 10 °C min⁻¹: (a) measured TG curves of SS, CS and their blends; (b) measured and theoretical TG curves of the blends; (c) interaction deviation, $\Delta W = W_{\text{exp}} - W_{\text{cal}}$. $\Delta W < 0$ indicates enhanced mass loss; $\Delta W > 0$ indicates inhibited mass loss or enhanced solid retention

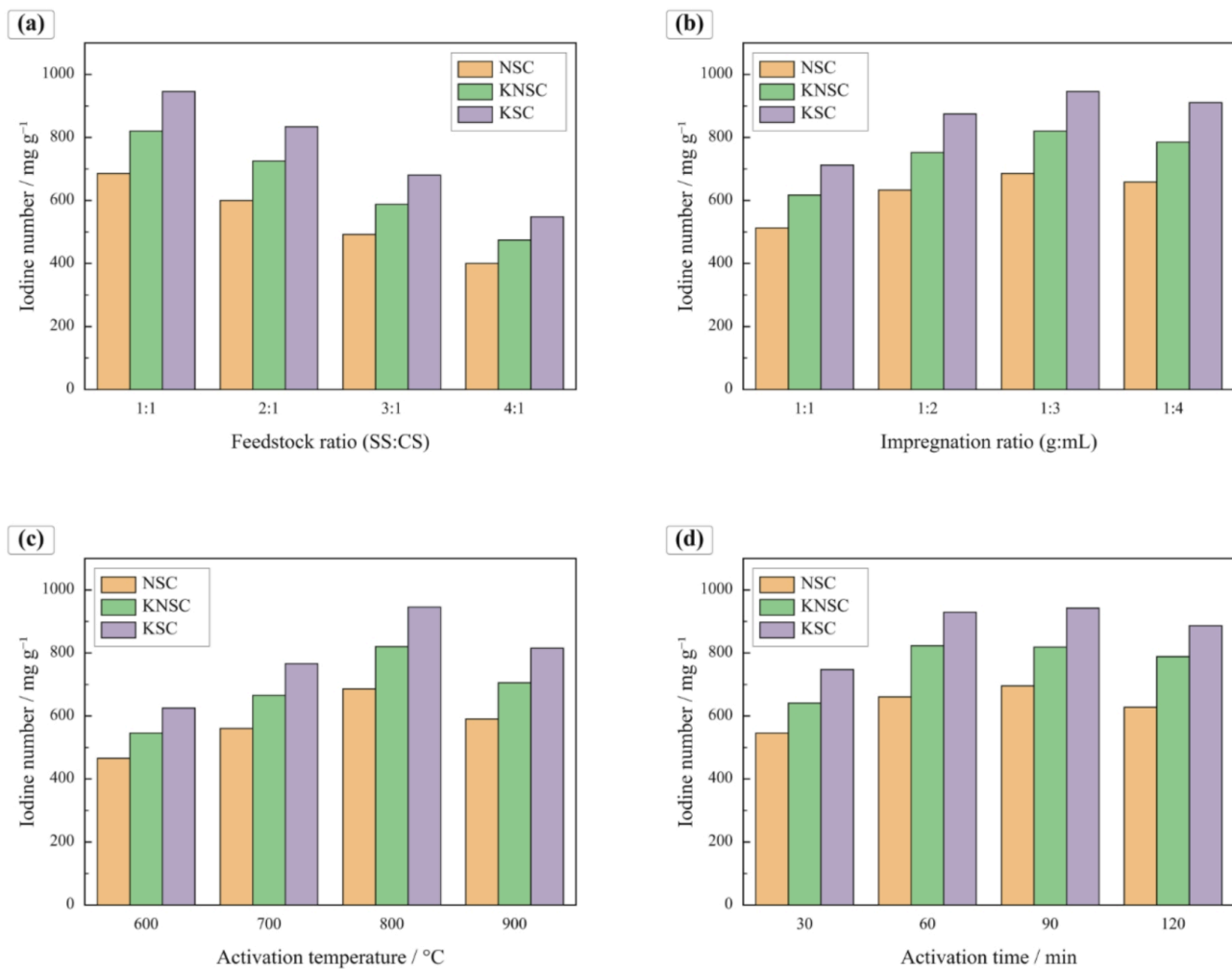


Figure 2

Effects of feedstock ratio, impregnation ratio, activation temperature and activation time on iodine number and the selected process conditions

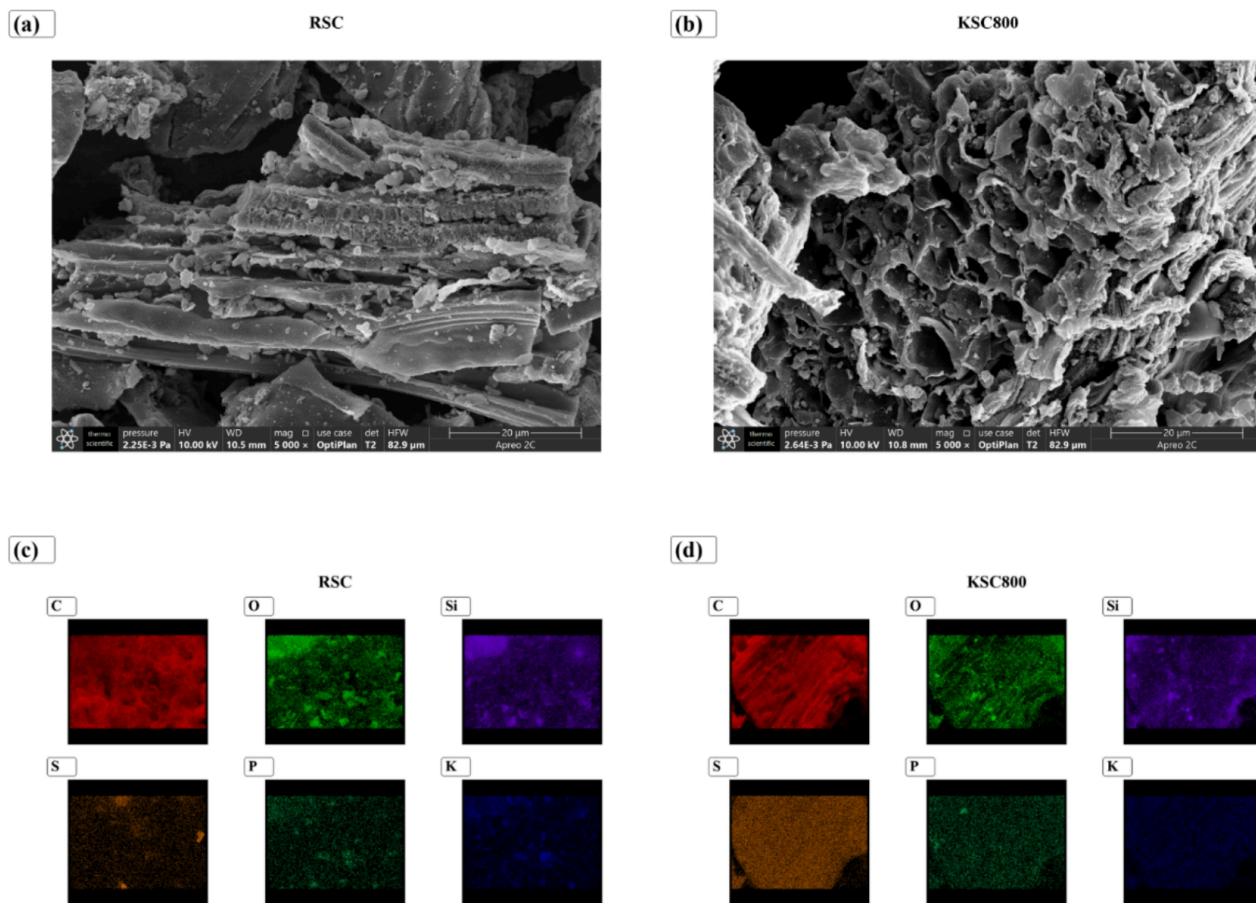
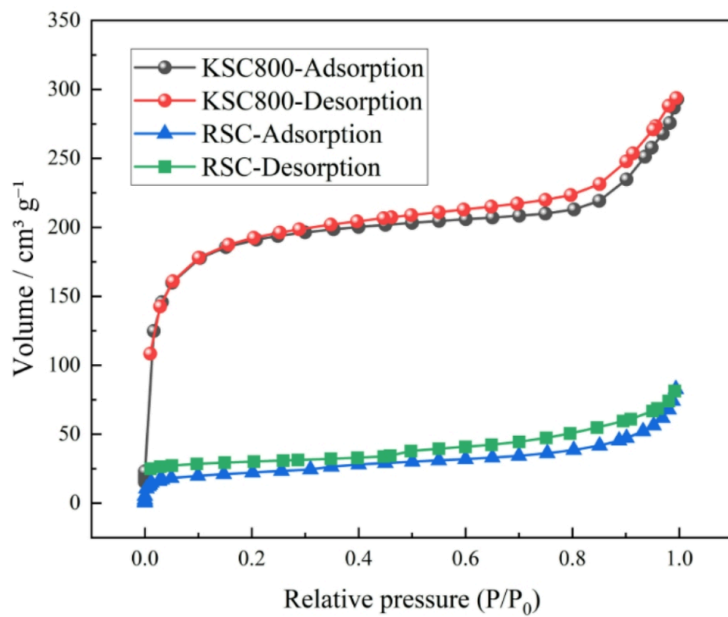


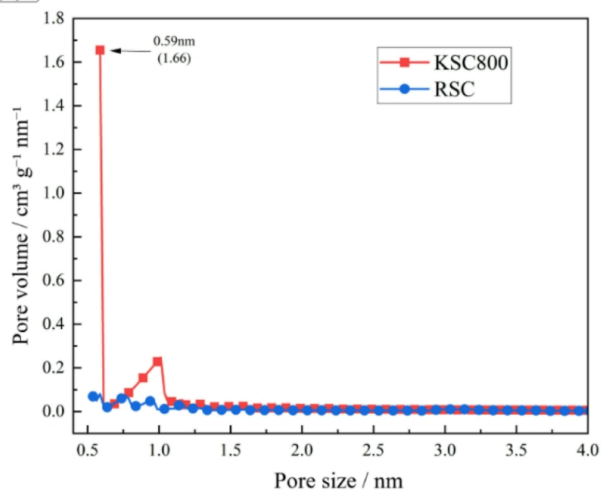
Figure 3

Surface morphology and elemental maps of RSC (a, c) and KSC800 (b, d)

(a)



(b)



(c)

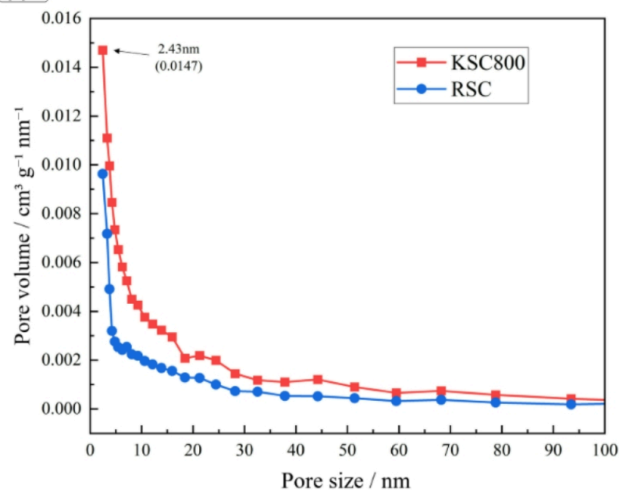


Figure 4

N₂ adsorption-desorption isotherms and pore size distributions of RSC and KSC800

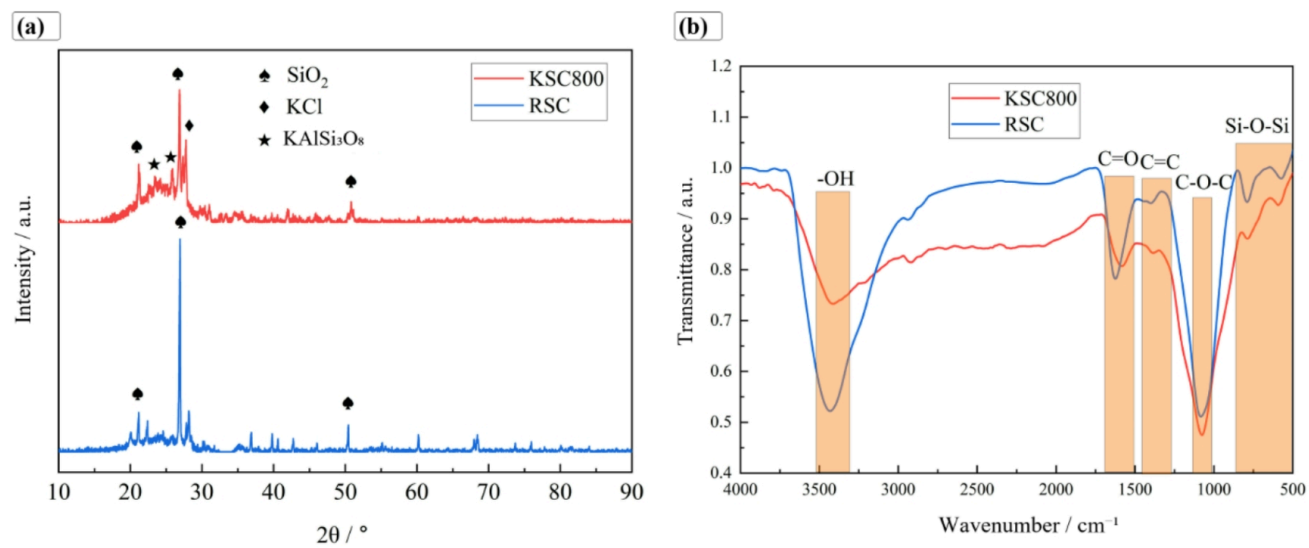


Figure 5

XRD patterns and FTIR spectra of RSC and KSC800

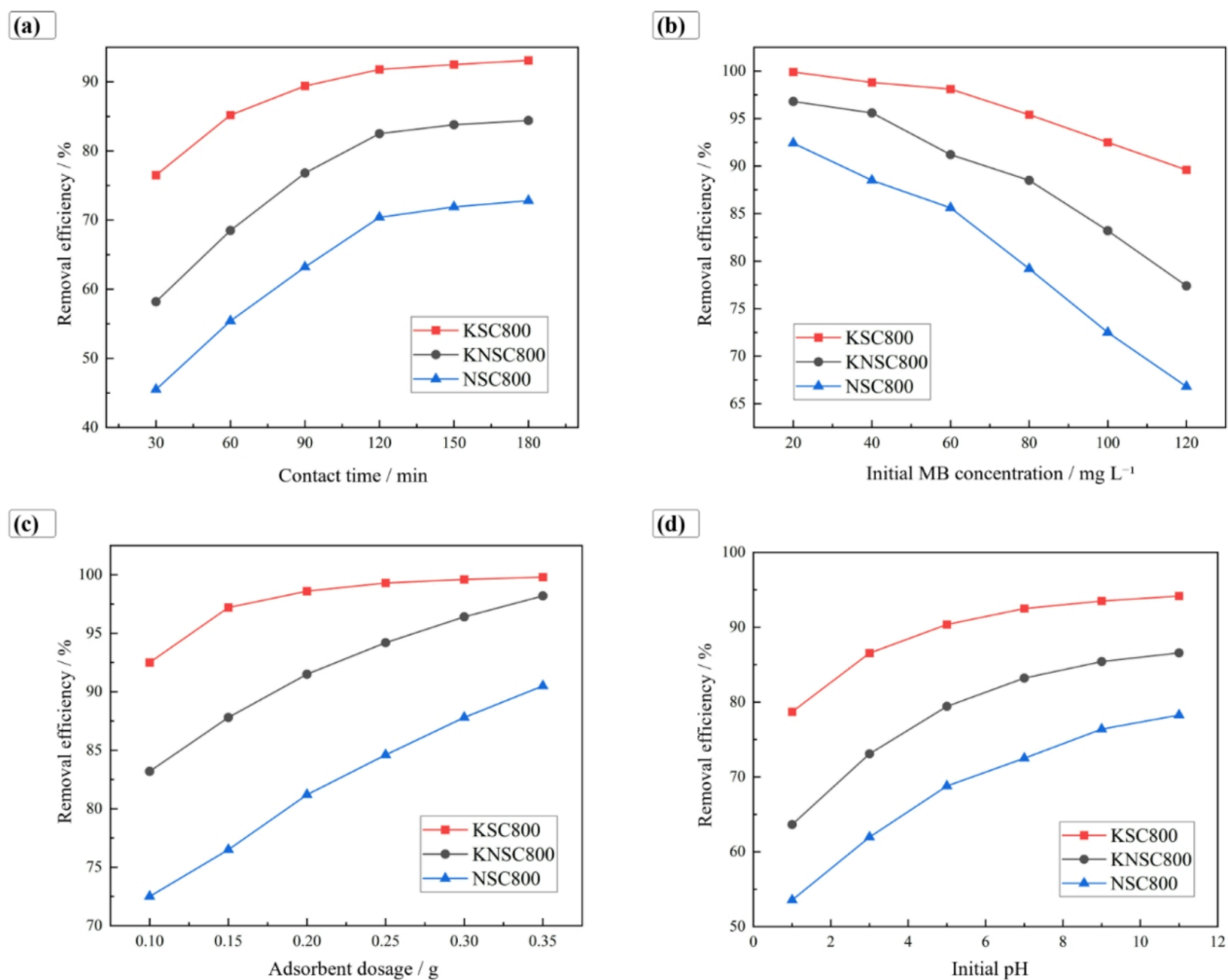


Figure 6

Effects of contact time, initial MB concentration, adsorbent dosage and initial pH on MB removal by KSC800, KNSC800 and NSC800

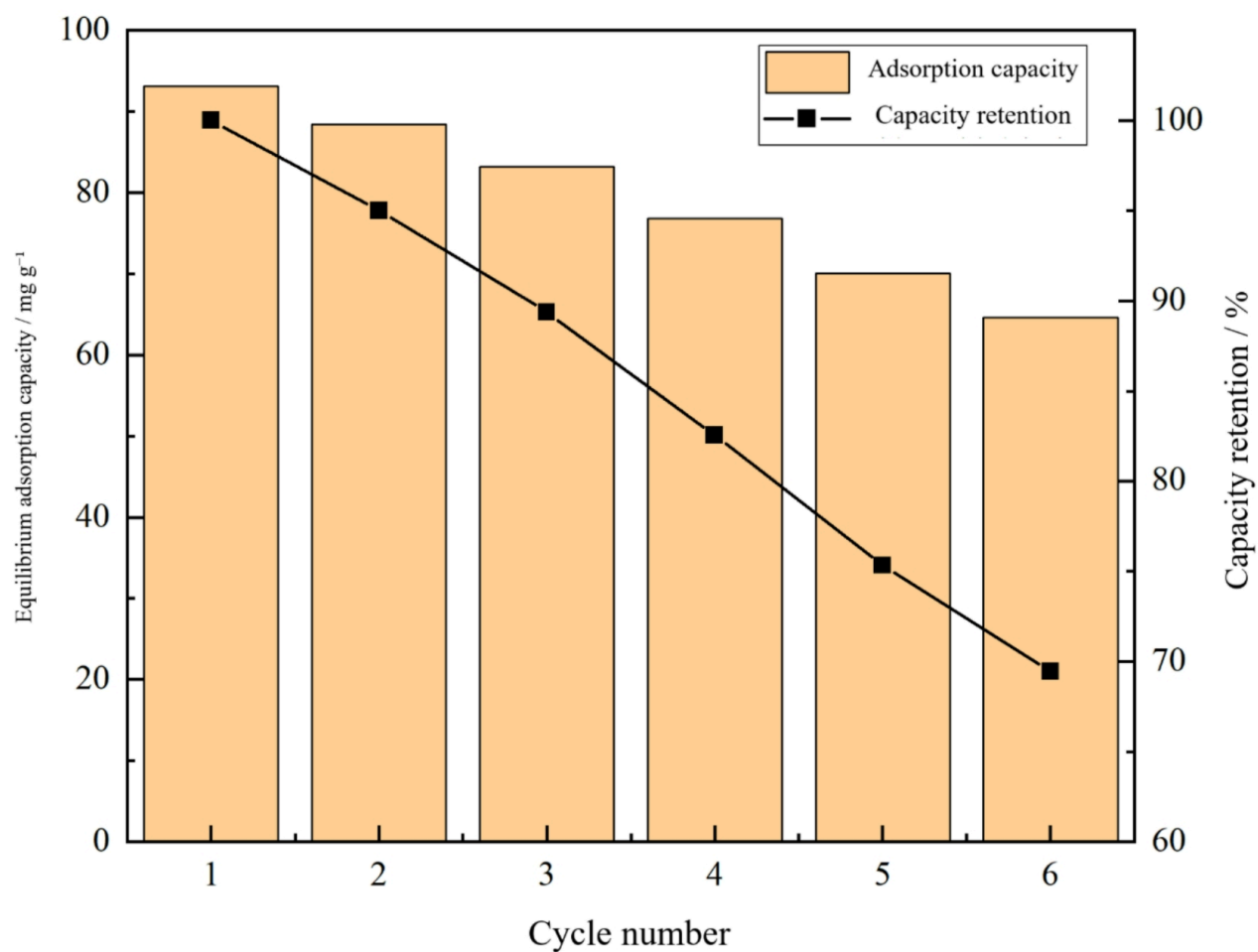


Figure 7

Equilibrium adsorption capacity of KSC800 during repeated adsorption–desorption and capacity retention relative to initial use. Cycle 1 denotes initial use, and cycles 2–6 denote use after the first through fifth regenerations