RESEARCH

Open Access

Enhanced adsorption of phenol using EDTA-4Na- and KOH-modified almond shell biochar

Yanqin Chen^{1*}, Donghui Wang², Xueli Wang², Jing Wu² and Shifang Song²

Abstract

To enhance the performance of biochar made from almond shells for adsorption of phenol pollutants in water, we prepared an almond shell-based biochar and modified it through combined pyrolysis with KOH and EDTA-4Na at 750 °C, yielding almond shell-based modified activated carbon (A-BC); the mass ratio of biochar, EDTA-4Na, and KOH was 1:1:3.

A-BC was characterized by using Scanning Electron Microscopy, Fourier Transform Infrared Spectroscopy, the Brunauer–Emmett–Teller method, and X-ray Diffraction. The adsorption conditions of A-BC for phenol were optimized through single-factor experiments, and the adsorption mechanism was explored through kinetics and thermodynamics assays. The results show that A-BC exhibits a honeycomb-like structure with a specific surface area of 1050 m² g⁻¹ and a micropore ratio of 86%. A-BC is rich in functional groups (-OH, -CH₂, N–C, C-H, N–H) closely related to phenol adsorption. The adsorption of phenol by A-BC is a spontaneous exothermic process involving both physical adsorption and chemical adsorption (including hydrogen bonding and π - π interactions). The pseudo-second-order kinetic model adequately describes the adsorption process, which consists of liquid film diffusion, surface adsorption, and intraparticle diffusion stages. At 25 °C, with an A-BC dosage of 1.0 g L⁻¹, initial phenol concentration of 400 mg L⁻¹, and contact time of 60 min, A-BC exhibited significant adsorption capacities of 161 and 149 mg g⁻¹ for simulated water and phenol-containing wastewater from coal chemical industries, respectively. A-BC demonstrated good reuse performance and strong adsorption capacity for phenol, indicating its potential application in treating phenol-containing wastewater from coal chemical industries.

Keywords Biochar, Modification, Almond shell, Adsorption, Phenol

1 Introduction

As a fundamental chemical raw material, phenol is widely used in petrochemical, coal processing, papermaking, electroplating, dyeing, and pharmaceutical industries. Due to its significant toxicity and bioaccumulation potential, phenol has been listed among the pollutants for global priority control [1]. Domestic enterprises discharge approximately 40 BT of industrial wastewater annually, with phenol-containing industrial wastewater accounting for about 0.5%, or 200 MT. Current methods for treating phenol-containing wastewater include membrane filtration, photocatalytic degradation, advanced oxidation processes, biodegradation, and adsorption [2]. Among these, adsorption is highly efficient, costeffective, and simple to operate, making it a promising method for removing phenol from wastewater [3].

In phenol adsorption research, biochar has attracted significant attention due to its well-developed porous structure, easily modifiable carbon chemistry, abundant surface functional groups, and high ion-exchange capacity [4, 5]. However, the pore volume and specific surface



© The Author(s) 2025. **Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

^{*}Correspondence:

Yanqin Chen

xjdxcyq@sohu.com

¹ Xinjiang Key Laboratory of Agricultural Chemistry and Biomaterials,

Xinjiang Agricultural University, Urumqi 830052, China

² College of Chemistry and Chemical Engineering, Xinjiang Agricultural University, Urumqi 830052, China

area of biochar are typically low due to the limitations of biomass feedstock properties; therefore, researchers have focused on modifying biochar by enhancing its pore structure and altering its surface functional groups to improve its adsorption capacity. Research has found that modifying biochar not only enhances its performance in removing pollutants from water [6], but also improves the adsorption of heavy metals [7], improves soil quality by increasing soil microbial diversity [8, 9], can be used to prepare electrodes [10], and serves as a feed additive [11]. Modified biochar shows promise as an adsorbent for removing phenol from contaminated wastewater (Table 1). It has been found that KOH activation can enhance biochar's pore structure at high temperatures under which KOH reacts with carbon to produce H_2 and the intermediate product, K_2CO_3 , which further reacts to generate CO_2 , CO, K_2O , etc. KOH, K_2CO_3 , and K_2O can etch the carbon skeleton of biochar, increasing its roughness and specific surface area, while H_2 , CO_2 , and CO form a rich micro/mesoporous structure and high specific surface area when released from the biochar [44]. Organic salts can also alter the composition and functional groups of biochar through chemical reactions applied EDTA-4Na to introduce N elements in situ, which increased the electron mobility and hydrophobicity of biochar, while also enhancing the number of

Table 1 Comparison of the performance of modified carbon prepared from pyrolysis of agricultural waste materials in removing phenol from wastewater (main literature published in 2022–2024)

Biomass	Modifier	Qe (mg g^{-1})	Year	References
Acacia mangium	H ₃ PO ₄	54	2023	[12]
sugarcane bagasse	H ₂ SO ₄	159	2022	[13]
sugarcane bagasse	HNO ₃	588	2023	[14]
oak wood	H ₃ PO ₄	250	2024	[15]
Brazil nutshell	КОН	69	2022	[16]
sunflower	CO_2 , water vapor, $C_6H_{12}N_2$	190	2022	[17]
reed stems	FeCl ₃ , ZnCl ₂	63	2023	[18]
coconut shell carbon	NaOH	300	2022	[19]
rice hulls	H ₃ PO ₄	15	2022	[20]
fox nutshell	H ₃ PO ₄	102	2024	[21]
coffee grounds	H ₃ PO ₄	24	2022	[22]
sugarcane bagasse	ZnCl ₂	9	2023	[23]
wheat straw	HF, CO ₂	471	2023	[24]
olive pits	ZnCl ₂	120	2024	[25]
corn straw	КОН	612	2023	[26]
oak wood	H ₃ PO ₄	250	2023	[27]
bamboo	ZnCl ₂	61	2023	[28]
bamboo	ZnCl ₂ , FeCl ₃ , KOH	459	2023	[29]
bamboo	H ₂ O, K ₂ FeO ₄ , CaCO ₃ , NH ₃	212	2023	[30]
cactus cladode powder	$Na_3C_6H_5O_7$, FeCl ₃ , CH ₃ COONa, (CH ₂ OH) ₂	175	2023	[31]
groundnut shells	CoCl ₂ , ZnCl ₂	127	2024	[32]
wheat straw	NH ₃ , HCI	177	2023	[33]
Brazil nutshells	КОН	99	2023	[34]
palm kernel shells	КОН	7	2023	[35]
Hevea brasilliensis seeds	KOH, HCI	13	2023	[36]
sugarcane	NaOH	109	2023	[37]
sugarcane officinarum	ZnCl ₂	65	2023	[38]
<i>Eucalyptus saligna</i> sawdust	NiCl ₂	77	2024	[39]
coconut shell	K ₂ CO ₃	25	2024	[40]
Camellia oleifera seed hulls	K ₂ CO ₃	300	2024	[41]
rice hulls	KOH, Na ₂ EDTA	195	2024	[42]
sunflower stems	КОН	333	2024	[43]

pyridinic-N (N-6) functional groups, thus improving the biochar's phenol adsorption capacity [45]. However, previous studies on improving biochar's adsorption of phenol or other organic pollutants through modification have primarily focused on either its pore structure or surface functional groups, with few studies addressing both simultaneously. Therefore, modifying both biochar's pore structure and the surface functional groups holds promise for enhancing its application potential in organic pollutant adsorption technologies.

Almonds are an important economic crop with global demand increasing annually. In 2023, the global production reached approximately 1.6 MT. However, the large-scale utilization of almond shells, which are often discarded as waste, has not yet been formally reported. Almond shells have a large surface area, many pores, and low ash content, making them an ideal raw material for biochar production. Encinas-Vazquez et al. [46] prepared almond shell biochar that achieved a maximum lead adsorption capacity of 40 mg g^{-1} from water; Alves et al. [47] prepared almond shell biochar with a maximum cadmium adsorption capacity of 5.8 mg g⁻¹; Maaloul et al. [48] prepared modified almond shell adsorbents with a copper adsorption capacity of 18 mg g⁻¹ from water; Wang et al. [49] prepared biochar via a one-step pyrolysis method with a maximum phenol adsorption capacity of 11 mg g^{-1} . Given the relatively low adsorption capacity of unmodified almond shell biochar, modifying it to enhance its adsorption performance for use in treating water pollutants is significant for pollution reduction and carbon emission mitigation.

The goal of this study was to improve the performance of biochar in the treatment of phenol-containing wastewater and explore its potential for application in industry, especially in the treatment of phenol-containing wastewater from the coal chemical industry. We characterized and tested almond shell-based biochar prepared by one-step pyrolysis with a combination of KOH and EDTA-4Na at high temperature. Phenol, a water pollutant, is used as the target substance to explore the relationship and mechanism between the biochar's structure and phenol adsorption performance. This research aims to provide theoretical guidance for the integrated preparation of chemically activated-modified biochar, technical support for using almond shells and similar agricultural waste in the preparation of activated carbon materials for adsorbing organic pollutants in water bodies, and insights for waste treatment and carbon emission reduction.

2 Materials and methods

2.1 Raw materials and reagents

Almond shells: The almond shells, sourced from Shache County, Kashgar, Xinjiang, were separated from the kernels. The shells were washed with distilled water to remove surface dust and other impurities, dried at 85 °C, crushed, and sieved through a 140-mesh sieve (0.015 mm) for later use.

Actual water samples: The water samples were collected from untreated wastewater of a coal chemical enterprise in Junggar, Xinjiang. The contents measured were as follows: phenolic compounds at 3000 g L⁻¹, phenol at 1350 mg L⁻¹, suspended solids at 43 mg L⁻¹, chloride ions at 2835 mg L⁻¹, COD at 3867 mg L⁻¹, ammonia nitrogen at 325 mg L⁻¹, and a pH of 7.58.

Pretreatment of actual water samples: A certain volume of the actual water sample was taken and centrifuged at 5000 rpm for 10 min in a centrifuge (H1850, Hunan Xiangyi Laboratory Instrument Development Co.) to remove suspended solids. Chloride ions were precipitated using a 0.10 M AgNO₃ solution, and the precipitate was further removed by centrifugation at 5000 g. This process was repeated until the chloride ion content in the actual water sample was less than 10 mg L⁻¹; the resulting sample was then prepared for analysis.

Reagents: All reagents used were of analytical grade. Anhydrous ethanol (CH₃CH₂OH) was sourced from Tianjin Xinbote Chemical Co. Phenol (C₆H₅OH) was obtained from Tianjin Zhiyuan Chemical Reagent Co. Sodium hydroxide (NaOH) was acquired from Tianjin Zhiyuan Chemical Reagent Co. Hydrochloric acid (HCl) was provided by Sichuan Xilong Chemical Co. EDTA-4Na (C₁₀H₁₂N₂O₈Na₄·4H₂0) was purchased from Shanghai Titan Scientific Co.

2.2 Biochar preparation and modification

2.2.1 Biochar preparation

A weighed sample of almond shell powder was placed in a covered magnetic boat and transferred to a tube furnace (GSL-1600X, Hefei Kejing Materials Co.) for pyrolysis to produce almond shell biochar. The pyrolysis temperature was 400 °C with a heating rate of 5 °C min⁻¹, the time was 120 min, and the nitrogen flow rate was 100 mL min⁻¹.

2.2.2 Preparation of modified carbon

Following the method of Lv et al. [45], biochar, EDTA-4Na, and KOH were mixed in the ratio of 1:1:3 and placed in a tube furnace for pyrolysis. The pyrolysis was done at 750 °C for 60 min, with a heating rate of 5 °C min⁻¹, and a nitrogen flow rate of 100 mL min⁻¹. The product obtained after pyrolysis was modified activated carbon (A-BC).

2.3 Properties of biochar

To determine the changes in surface groups before and after modification, Fourier transform infrared spectroscopy (FTIR Prestige-21, Shimadzu, Japan) was used to analyze biochar and A-BC. Spectrally pure KBr powder was used for background, with the resolution maintained from 1 to 4 cm⁻¹, and a scanning range of 400 to 4000 cm⁻¹. The signals were converted using the K-M method.

To characterize the morphology and pore structure of the materials before and after modification, a field-emission scanning electron microscope (SEM, Zeiss, Gemini 300, USA) was used to examine biochar and A-BC. For the measurement, samples were directly attached to conductive adhesive and coated with gold. The acceleration voltage was set to 3 kV for observing the morphology.

To determine the specific surface area, pore volume, and pore size distribution of biochar and A-BC before and after modification, an automated surface area and porosimetry analyzer (Micromeritics APSP 2460, USA) was employed. Nitrogen was used as the adsorbate gas, with a degassing temperature of 200 °C and a degassing time of 8 h. The Barrett-Joyner-Halenda model and Brunauer–Emmett–Teller (BET) model were used to analyze the pore size distribution.

To determine the crystal phase structure of the materials, X-ray diffraction (XRD) analysis was performed on biochar and A-BC using an X-ray diffractometer (D8 Advance, Germany). Cu K α radiation (λ =0.15 nm) was used, with a tube voltage of 40 kV and a tube current of 40 mA. The scanning speed was set to 5° min⁻¹, and data were collected over an angular range of 10 ~ 80°.

2.4 Adsorption experiment

2.4.1 Phenol adsorption

The adsorption experiment was conducted in 50 mL conical flasks with glass stoppers. A weighed sample of 0.0400 g of A-BC was added to 20 mL of a 400 mg L^{-1} phenol solution. The mixture was placed in a constant temperature water bath oscillator (SHA-C, Jintan Medical Instruments Factory, China) at a stirring speed of 150 rpm for 240 min. After adsorption, the phenol solution was filtered, and the absorbance of the filtrate was measured at 270 nm. The adsorption efficiency and adsorption capacity of A-BC were calculated using formulas (1) and (2). Each experiment was conducted in triplicate.

$$R = \frac{C_0 - C_e}{C_0} \times 100\%$$
 (1)

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

where, R: adsorption efficiency, %; Q_e : adsorption capacity at equilibrium, mg g⁻¹; C_0 : initial concentration of phenol before adsorption, mg L⁻¹; C_e : equilibrium concentration of phenol after adsorption, mg L⁻¹; V: volume of phenol solution, L; and M: weight of biochar, g.

2.4.2 Optimization of adsorption conditions

The effects of the amount of A-BC, initial solution pH, initial phenol concentration, and contact time on the adsorption of phenol by A-BC were investigated. The amount of A-BC ranged from 0.5 to 3.0 g L⁻¹ and the initial pH of the solution was adjusted to between 2 and 12 using 0.1 M HCl and 0.1 M NaOH solutions. The initial phenol concentration in the solution was between 10 and 400 mg L⁻¹, and the contact time was 0 to 360 min. After each set of experiments, the A-BC was removed from the solution by centrifugation (5500 *g* force, 25 °C, 15 min) and filtered through a 0.45 µm membrane before measurement.

2.4.3 Adsorption kinetics and thermodynamics

The pseudo-first-order and pseudo-second-order kinetic models, and the intraparticle diffusion model were tested for fitting the kinetic process of phenol adsorption by A-BC. The Langmuir, Freundlich, and Sips models were used to fit the thermodynamics of phenol adsorption by A-BC from the solution. The Gibbs free energy (Δ G), enthalpy (Δ H), and entropy (Δ S) for the adsorption process were calculated. The model calculations used are shown in Eqs. (3)–(11).

Pseudo-first order:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \tag{3}$$

Pseudo-second order:

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \tag{4}$$

Intraparticle diffusion:

$$Q_{t} = k_{P}\left(t^{0.5}\right) + C \tag{5}$$

Langmuir isotherm:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{max}} + \frac{1}{K_l \cdot Q_{max}}$$
(6)

Freundlich isotherm:

$$\lg Q_e = \lg K_F + \frac{1}{n} \lg C_e \tag{7}$$

Sips isotherm:

$$Q_e = \frac{Q_{max}K_s(C_e)^N}{1 + K_s(C_e)^N}$$
(8)

$$\Delta G^0 = -RT ln K_d \tag{9}$$

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{10}$$

$$K_d = K_l \times M_{phenol} \times M_{H_2O} \times 1000 \tag{11}$$

where, Q_t : amount of phenol adsorbed by almond shell biochar at time t, mg g⁻¹; Q_{max} : maximum adsorption capacity of almond shell biochar, mg g⁻¹; k_1 : pseudofirst-order adsorption rate constant, min⁻¹; k_2 : pseudosecond-order adsorption rate constant, g mg⁻¹ min⁻¹; k_p : intraparticle diffusion rate constant, mg g⁻¹ min^{-0.5}; C: boundary layer thickness constant; K_I , K_F and K_s : adsorption equilibrium constants, L mg⁻¹; n: adsorption constant; N: heterogeneity coefficient; R: gas constant, 8.314 J mol⁻¹ K⁻¹; T: temperature, K; and K_d : equilibrium constant.

2.4.4 Reusability of A-BC

After reaching adsorption saturation, A-BC was separated and placed in 50 mL of distilled water. It was then shaken in a constant temperature oscillator (25 °C, 180 rpm) for 120 min to desorb phenol. The phenol concentration in the solution was measured, and the process was repeated until no additional phenol was detected in the solution. The desorbed A-BC was reused five times following the procedure in Sect. 2.4.2 to evaluate its regeneration performance and reusability.

2.4.5 Actual water sample determination

The pretreated water sample was diluted by half. A 20 mL aliquot of the diluted sample was taken, and the test was conducted following the procedure in Sect. 2.4.1 to verify the adsorption performance of A-BC on phenol in wastewater from a coal chemical company.

2.4.6 Data processing

Data input and calculations were performed using Microsoft Excel 2010. For data organization, plotting, and statistical analysis, Origin 2019 was employed. Single-factor analysis of variance and standard deviation calculations were based on the results from three replicate experiments. A *P*-value of less than 0.05 (P < 0.05) indicates a statistically significant difference between means.

3 Results and discussion

3.1 Characterization of A-BC 3.1.1 FT-IR

The FT-IR spectra of A-BC and biochar (Fig. 1) show a strong, broad peak at 3440 cm⁻¹ for both, which is attributed to the -OH bond, resulting from the stretching vibration of alcohol phenols, possibly originating from the cellulose in the material [50]. The characteristic peaks at 2930 and 2950 cm⁻¹ correspond to the asymmetric and symmetric stretching vibrations of -CH₂, related to hemicellulose and cellulose, but the peak shape is more pronounced in biochar, indicating that the cellulose content in A-BC gradually decreased during high-temperature carbonization. A-BC shows distinct absorption peaks between 1630 and 1527 cm⁻¹, corresponding to amide N-H stretching vibrations, indicating that EDTA-4Na successfully modified the original biochar functional groups through amide reactions [51]. The bending vibration at 1090 cm⁻¹ corresponds to N-C and the out-ofplane bending vibration at 958 cm⁻¹ shows changes in peak shape, further verifying the successful modification of biochar by EDTA-4Na [51, 52]. The surface of A-BC, with its strong aromatic C-H, N-C, and N-H functional groups, can provide electron donors to bind pollutants [53].

3.1.2 SEM

The SEM images of A-BC and biochar (Fig. 2) show that biochar has a smooth surface with micropores and contains many wrinkled, flake-like, and blocky structures. A-BC displays a honeycomb microstructure due to the pore-forming effect of KOH at high temperatures [49, 54]. The reaction of EDTA-4Na with inorganic substances in the raw material during carbonization forms organic metal salts that expand the pore volume of the raw material and increase the distance between carbon microcrystals [45, 53]. Combined with nitrogen adsorption-desorption data, it is evident that the multilayer pore structure on the surface of A-BC increases its specific surface area, with a significant distribution of mesopores inside the A-BC particles. These mesopores provide more space for the adsorption, enrichment, diffusion, and migration of phenol. The newly formed macropores on the outer surface facilitate the formation of new mesopores and micropores on the inner surface [54]. The interconnected open-mode micropore structure can promote mass transfer processes, thereby enhancing the adsorption capacity of A-BC for phenol. The layered Energy-dispersive X-ray spectroscopy (EDS) images of A-BC (Fig. 2c) show that the elements C and Na are uniformly distributed on A-BC. Based on the EDS spectral data in Fig. 2d, we concluded that A-BC was



Fig. 1 FT-IR spectra of A-BC and biochar. Test conditions: spectral grade KBr powder for background, resolution of 1–4 cm⁻¹, and scanning range of 400–4000 cm⁻¹



Fig. 2 Scanning electron micrographs of biochar (a), A-BC (b) and EDS Layering of A-BC (c). d EDS information of A-BC. The particles were sputtered with gold and the imaging voltage was 3 kV



Fig. 3 Nitrogen adsorption-desorption and pore size distribution curves of biochar (a) and A-BC (b). The adsorption gas was N₂, the adsorption-desorption temperature was –196 °C, and the degassing time was 8 h

mainly composed of C (99.86%) and Na (0.14%), indicating a high degree of carbonization. This extensive carbonization ensures the stability and reliability of A-BC as an adsorbent [55]. The uniform distribution of Na on the A-BC surface also confirms the successful modification of biochar by EDTA-4Na.

3.1.3 BET

The isothermal adsorption-desorption curves of biochar and A-BC in Fig. 3 indicate that the N₂ adsorption capacity of both biochar and A-BC increases as the relative pressure P/P_0 increases. At a relative pressure of 0.8, the adsorption and desorption curves do not coincide, indicating a Type IV isotherm according to the Brunauer-Deming-Deming-Teller classification. The typical characteristic of particles with Type IV isotherms is the coexistence of micropores and mesopores, suggesting that both biochar and A-BC possess a mixed microporous-mesoporous structure [56]. Figure 3 further reveals that the pore size distribution of biochar ranges from 5 to 40 nm, with a relatively abundant presence between 5 and 25 nm, which is dominated by mesopores. In contrast, the pore size distribution of A-BC is primarily within the 1.5 to 3.0 nm range, dominated by micropores, but exhibiting both microporous and mesoporous characteristics. Taken together, our results support the hypothesis that the experimental method employed in this study is suitable for the preparation of microporous biochar [45].

The specific surface area and pore structure directly influence the adsorption performance of biochar. As shown in Table 2, the specific surface area and pore volume of A-BC prepared by the integrated KOH

 Table 2
 Specific surface area and pore structure characteristics

 of biochar and A-BC
 Image: Specific surface area and pore structure characteristics

Sample	$f A_{BET}^{} (m^2 g^{-1})$	V _{total} (cm ³ g ⁻¹)	V _{mic} (cm ³ g ⁻¹)	V _{mic} /V _{total}	Dp (nm)
A-BC	1050	0.42	0.36	86%	1.6
biochar	2	0.0029	0.00096	32%	5.1

 A_{BET} specific surface area (m² g⁻¹), *Vtotal* total pore volume (cm³ g⁻¹), V_{mic} micropore volume (cm³ g⁻¹), V_{mic}/V_{total} ratio of micropore volume to total pore volume, *Dp* pore diameter (nm)

activation and EDTA-4Na modification method have both significantly increased. The specific surface area increased from 2.3 to 1050 $m^2 g^{-1}$, and the pore volume increased from 0.0029 to 0.42 cm³ g⁻¹. A-BC is primarily microporous, with micropores accounting for 86% of the total and an average pore diameter of 1.6 nm. A higher proportion of micropores provides more surface area for adsorption and attachment points for small molecules and volatile organic compounds [57]. The significant changes in specific surface area and pore volume of A-BC may be due to the erosion of the carbon lattice by KOH vapor at high temperatures, accelerating the breaking of C-H, hydroxyl, and carboxyl bonds in lignocellulose, which promotes pore formation [45]. Additionally, during high-temperature carbonization, the reaction of KOH with carbon produces H₂, CO₂, and CO, and the decomposition of EDTA-4Na generates CO, CO₂, and nitrogen oxides. The release of these gases from the interior and surface of biochar also contributes to the formation of pore structures [45].



Fig. 4 XRD patterns of biochar and A-BC. Test conditions: Cu Ka radiation (λ = 0.15 nm); tube voltage, 40 kV; tube current 40 mA; scanning speed 5° min⁻¹

3.1.4 XRD patterns

The XRD pattern of A-BC (Fig. 4) shows only broad peaks, indicating a higher degree of amorphousness [58]. The diffraction peak at $2\theta = 12.6^{\circ}$ (101) is attributed to cellulose, and the higher intensity of this peak in biochar compared to A-BC is due to the decomposition of cellulose during the modification process [59]. The diffraction peak at $2\theta = 29.4^{\circ}$ (C002) corresponds to the characteristic peak of SiO₂, while the broad amorphous peak at $2\theta = 40^{\circ}$ (C100) indicates the formation of an amorphous graphite structure, which is conducive to adsorption [60].

3.2 Preparation of A-BC

To select the appropriate amount of modifier to add, biochar modification was performed with reference to the method of Lv et al. [45] and the preliminary test results. Three different ratios of biochar:KOH:EDTA-4Na were tested for A-BC preparation, namely, 1:3:1, 1:3:2, and 1:3:3 (Fig. 5). Figure 5 indicates that when the ratio of biochar:KOH:EDTA-4Na is 1:3:1, the prepared A-BC exhibits the maximum adsorption capacity for phenol at 163 mg g⁻¹, with an adsorption rate of up to 83%. Therefore, for subsequent adsorption experiments, a biochar:KOH:EDTA-4Na ratio of 1:3:1 was selected for A-BC preparation. In this study, the adsorption capacity of A-BC for phenol in simulated wastewater was lower than that of the rice hull-based activated carbon prepared by Lv et al. [45]. This difference is related to the honeycomb-like structure of the A-BC prepared in this study, compared to the tubebundle shape of the rice hull-based activated carbon prepared by Lv et al. This structural difference may be attributed to the varying proportions of cellulose, hemicellulose, and lignin in rice hulls and almond shells.

3.3 Adsorption experiment 3.3.1 Effect of A-BC dosage

Figure 6 illustrates that compared to biochar, the adsorption performance of A-BC for phenol was significantly increased. With an increase in A-BC ranging from 0.5 to 3 g L^{-1} , the efficiency of phenol adsorption increased from 37 to 98%, while the adsorption capacity decreased from 287 to 127 mg g⁻¹. This trend aligned with findings by Allahkarami et al. [61]. The increase in adsorption efficiency with higher A-BC amounts can be attributed to the availability of more active binding sites for phenol. However, the mass of phenol adsorbed per unit mass of A-BC decreased as A-BC was increased, indicating that the driving force for mass transfer at the liquid-solid interface did not increase significantly with higher A-BC dosage. Based on these results and considering practical applications, 1.0 g L⁻¹ A-BC was used in subsequent experiments.



Fig. 5 Influence of different ratios of pyrolysis materials (biochar, KOH, EDTA) on adsorption. For preparation, the pyrolysis temperature was 750 °C, the time was 60 min, the nitrogen gas flow rate was 100 mL min⁻¹, and the heating rate was 5 °C min⁻¹



Fig. 6 Effect of A-BC dosage on phenol adsorption. Experimental conditions: A-BC dosage, 0.5–3.0 g L⁻¹; initial phenol concentration, 400 mg L⁻¹; initial pH of the solution was not adjusted; contact time, 240 min; solution volume, 20 mL; temperature, 25 °C

3.3.2 Effect of initial solution pH

Figure 7 demonstrates the influence of the initial pH on phenol adsorption by A-BC, indicating that

strongly acidic conditions are highly favorable for phenol adsorption. At an initial pH of 2 and an equilibrium time of 120 min, A-BC achieved a maximum



Fig. 7 Effect of initial pH on phenol adsorption by A-BC. Experimental conditions: A-BC dosage, 1.0 g L⁻¹; initial phenol concentration, 400 mg L⁻¹; initial pH of the solution ranging from 2 to 9; contact time, 240 min; solution volume, 20 mL; temperature, 25 °C

adsorption capacity of 177 mg g^{-1} . From pH 3 to 9, the variation in phenol adsorption capacity by A-BC was not significant, which is consistent with findings by Song et al. [60]. This suggests that the initial pH has a minimal impact on phenol adsorption by A-BC. The initial pH affected the surface charge of the adsorbent, thereby influencing its adsorption capacity. In strongly acidic solutions, where phenol is predominantly in its undissociated form, more phenol molecules were adsorbed onto the surface of A-BC. As the pH increased, the number of dissociated phenol molecules (phenolate ions) increased, leading to a decrease in A-BC's phenol adsorption capacity. When the initial pH of the phenol solution exceeded the pKa of phenol (pH=9.98), the surface of A-BC became negatively charged. This resulted in electrostatic repulsion between phenolate ions and the surface of A-BC, as well as phenol-phenolate ions in the solution, thereby reducing adsorption capacity until equilibrium was reached. The non-significant influence of initial solution pH on phenol adsorption by A-BC could also be attributed to the introduction of nitrogen-containing functional groups through EDTA-4Na modification. These functional groups form strong hydrogen bonds with phenol, thereby maintaining significant adsorption even under alkaline conditions [45, 58]. Based on these observations, subsequent experiments maintained the natural pH of the solution.

3.3.3 Effect of initial phenol concentration

Figure 8 illustrates that the adsorption capacity of A-BC for phenol is significantly enhanced compared to biochar. As the initial phenol concentration was increased from 10 to 1000 mg L^{-1} , the driving force for mass transfer between the liquid and solid phases intensified, resulting in an augmentation in the adsorption capacity. Specifically, when the initial phenol concentration in the solution was increased from 10 to 40 mg L^{-1} , the adsorption efficiency of A-BC for phenol rose from 96 to 99%, accompanied by an increase in adsorption capacity from 4.7 to 20 mg g^{-1} . However, as the initial phenol concentration was raised from 40 to 400 mg L^{-1} , the adsorption efficiency gradually decreased to 88%, while the adsorption capacity continued to grow, reaching 177 mg g^{-1} Beyond an initial phenol concentration of 400 mg L^{-1} , although the adsorption capacity of A-BC for phenol still increased, the adsorption efficiency declined markedly. At an initial phenol concentration of 1000 mg L^{-1} , the adsorption efficiency dropped to 35%. This phenomenon is primarily attributed to the fixed number of active binding sites on A-BC, where an increase in phenol concentration leads to competitive adsorption among phenol molecules on A-BC. To ensure optimal utilization of A-BC and maintain a suitable adsorption capacity and efficiency for phenol, the initial phenol concentration in subsequent experimental solutions was maintained at $400 \text{ mg } \text{L}^{-1}$.



Fig. 8 Effect of initial phenol concentration on phenol adsorption by A-BC. Experimental conditions: dosage of A-BC, 1.0 g L⁻¹; initial phenol concentration, 10–1000 mg L⁻¹; initial pH of solution unadjusted; contact time, 240 min; solution volume, 20 mL, temperature, 25 °C

3.3.4 Effect of contact time

Figure 9 illustrates the effect of contact time on phenol adsorption by A-BC. Initially (0–5 min), A-BC rapidly adsorbed phenol from the solution. At 5 min A-BC achieved an adsorption capacity of 152 mg g⁻¹ with an adsorption rate of 94%. As the contact time increased, the adsorption rate gradually decreased, reaching equilibrium around 60 min. At 60 min, A-BC exhibited an adsorption capacity of 161 mg g⁻¹ with an adsorption efficiency of 88%. During the initial stage of adsorption (0-5 min), A-BC's surface and micropores provided abundant active sites for phenol adsorption, resulting in minimal adsorption resistance. Phenol molecules were quickly adsorbed due to the availability of active sites. However, with prolonged contact time, the available active sites on the surface and within A-BC gradually decreased. As more phenol molecules were adsorbed, the resistance for subsequent phenol molecules to enter



Fig. 9 Effect of contact time on phenol adsorption by A-BC. Experimental conditions: dosage of A-BC, 1.0 g L⁻¹; initial phenol concentration, 400 mg L⁻¹, initial pH of solution unadjusted; contact time, 0–360 min; solution volume, 20 mL; temperature, 25 °C

deeper into the pores increased, leading to a decrease in adsorption rate until equilibrium was reached. Based on these findings, a contact time of 60 min was used in subsequent experiments to ensure that adsorption reached equilibrium.

3.4 Adsorption kinetics

Figure 10a and Table 3 present the fitting results of the kinetic models applied to the adsorption of phenol onto A-BC at 25 °C. The pseudo-second-order kinetic model shows a high correlation coefficient ($R^2 = 0.996$) with an equilibrium adsorption capacity (Q_e) of 160 mg g^{-1} . The pseudo-first-order kinetic model also exhibits a significant correlation coefficient ($R^2 = 0.982$) with a Q_e of 156 mg g^{-1} . These results indicate that the adsorption of phenol on A-BC most closely follows a pseudo-secondorder kinetic model. The pseudo-second-order kinetic model is established based on the theory of intermolecular interaction forces and surface reaction rates during the adsorption process. Consequently, functional groups such as -OH, N-H, C-O-C, and C=O on A-BC can undergo chemical adsorption through electron transfer, sharing, and the formation of hydrogen bonds. The pseudo-second-order kinetic model assumes that the adsorption rate is proportional to the square of the number of unoccupied sites on the adsorbent surface. Therefore, in this experiment, the adsorption rate of phenol onto A-BC is very fast during the initial stage of adsorption (0–5 min). Given that the correlation coefficient R^2 for the pseudo-first-order kinetic model is also relatively high, it indicates that while chemical adsorption of phenol onto A-BC occurs, it is accompanied by physical

 Table 3
 Kinetic fitting parameters for phenol adsorption by

 A-BC

Adsorption kinetics model	Fitting parameters	
The pseudo-first-order kinetic model	k ₁ /(min ⁻¹)	1.6
	$Q_e/(mg g^{-1})$	156
	R ²	0.982
The pseudo-second-order kinetic model	k ₂ /(g mg ⁻¹ min ⁻¹)	0.025
	$Q_e/(mg g^{-1})$	160
	R ²	0.996
The intraparticle diffusion model		
Stage 1	k _{p1} /(g mg ⁻¹ min ^{-0.5})	45
	C ₁	85
	R^2	0.992
Stage 2	k _{p2} /(g mg ⁻¹ min ^{-0.5})	6
	C ₂	142
	R^2	0.895
Stage 3	k _{p3} /(g mg ⁻¹ min ^{-0.5})	2
	C3	155
	R ²	0.610

adsorption mechanisms such as intermolecular forces and pore filling [51].

To determine the mass transfer process and ratelimiting steps in phenol adsorption on A-BC, an intraparticle diffusion model was employed for kinetic data analysis. Figure 10b and Table 3 illustrate the intraparticle diffusion process divided into three stages: liquid film diffusion, surface adsorption, and intraparticle diffusion.



Fig. 10 Kinetic model fitting of A-BC adsorption of phenol (**a**), and intraparticle diffusion model fitting (**b**). Experimental conditions: dosage of A-BC, 1.0 g L⁻¹; initial phenol concentration, 400 mg L⁻¹; initial pH of solution unadjusted; contact time, 0–360 min; solution volume, 20 mL; temperature, 25 °C



Fig. 11 Thermodynamics of phenol adsorption by A-BC. Experimental conditions: dosage of A-BC, 1.0 g L^{-1} ; initial phenol concentration, 400 mg L^{-1} ; initial pH of solution unadjusted; contact time, 0–360 min; solution volume, 20 mL; temperature, 25 °C

- **Stage 1 (0–5 min):** During this initial stage, the adsorption rate (k_{p1} =45 g mg⁻¹ min^{-0.5}) was at its highest due to hydrogen bonding and π - π interactions. Over 90% of phenol was adsorbed during this phase.
- Stage 2 (6–60 min): The adsorption rate decreased compared to Stage 1 $(k_{p1} > k_{p2})$. This decline may indicate that adsorption sites on A-BC were nearing saturation or the high-affinity active sites had been depleted.
- **Stage 3 (after 60 min):** Adsorption reached equilibrium, where the adsorption capacity remained nearly constant. Further adsorption of phenol molecules required overcoming increased mass transfer resistance to enter deeper into the pores of A-BC.

Additionally, the boundary layer effect (C_i values above 85 for all stages) significantly influenced the adsorption process. As the contact time increased, the boundary layer resistance increased, thereby slowing down the diffusion rate of phenol into the internal structures of A-BC [62].

3.5 Adsorption isotherms

The Langmuir, Freundlich, and Sips models are commonly used to describe adsorption processes, each with its own emphasis and scope of application. The Langmuir model is suitable for monolayer adsorption on a uniform surface, while the Freundlich model is an empirical model widely applied to various adsorption systems. The Sips model combines the characteristics of both, enabling a better description of non-ideal behaviors in complex adsorption systems. The fitting results of these three models to the experimental data of phenol adsorption onto A-BC at different temperatures are shown in Fig. 11 and Table 4. Table 4 indicates that all three models provide good fits at 25, 35, and 45 °C, with the Sips model exhibiting the highest R^2 value. Figure 11 also demonstrates that the Sips model aligns more closely with the experimental data, suggesting that it better fits the adsorption of phenol onto A-BC. The Sips adsorption model lies between the Langmuir and Freundlich models, incorporating the interactions between surface adsorption sites and the suitability for describing more complex multilayer adsorption systems. In this experiment, both pseudo-second-order and pseudo-first-order kinetic models fit well for the adsorption of phenol onto A-BC, consistent with the complex multilayer adsorption results from the Sips model fitting. Additionally, the N value in the Sips model ranges between 0 and 1 in this experiment, indicating that the adsorption of phenol onto A-BC is dominated by heterogeneous surfaces or pore

Table 4 Parameters of isothermal adsorption models

T/°C	25	35	45
Langmuir			
Κ _I	0.18	0.25	0.18
Q _{max}	199	184	171
R ²	0.983	0.971	0.987
Freundlich			
K _f	49	48	38
n	3.1	3.1	2.9
R ²	0.939	0.932	0.900
Sips			
Ks	0.20	0.24	0.18
Q _{max}	218	215	182
Ν	0.80	0.73	0.88
R ²	0.987	0.983	0.989

adsorption [61]. The honeycomb-like structure observed in the SEM image of A-BC further supports the conclusion that the adsorption of phenol by A-BC is primarily through heterogeneous surfaces and pore adsorption. Based on these findings, it can be preliminarily concluded that the adsorption of phenol by A-BC from solution belongs to heterogeneous adsorption, which involves the diffusion of phenol from the solution to the biochar surface, surface reactions, pore adsorption, and desorption of phenol from the biochar followed by re-diffusion into the solution.

3.6 Thermodynamics of adsorption

The thermodynamic data in Table 5 for phenol adsorption by biochar in solution shows that $\Delta G < 0$ at different temperatures, indicating that the adsorption of phenol onto A-BC from solution is a spontaneous process. This means that under the driving force of concentration, the phenol in solution tends to be adsorbed onto the surface of A-BC. The observation that $\Delta S > 0$ suggests an increase in randomness and disorder at the solid–liquid interface during phenol adsorption. This increase in disorder could be attributed to the transfer of phenol molecules or ions from a relatively ordered state in solution to the A-BC surface, where various potential adsorption sites may

 Table 5
 Thermodynamic parameters of adsorption.

Experimental conditions: dosage of A-BC, 1.0 g L⁻¹; initial phenol concentration, 400 mg L⁻¹; initial pH of solution unadjusted; contact time, 0–360 min; solution volume, 20 mL; temperature, 25 °C

Compound	ΔG (kJ mol ⁻¹)			ΔH (kJ mol ⁻¹)	ΔS (J K ⁻¹)	
	25 °C	35 °C	45 °C			
phenol	-3.35	-3.61	-3.75	-1.27	111	

exist, leading to a more disordered distribution of phenol molecules or ions on the A-BC surface. Additionally, the observation that $\Delta H < 0$ indicates that the adsorption of phenol onto A-BC from solution is an exothermic process. This may be due to the stronger interactions, such as van der Waals forces, hydrogen bonds, and electrostatic interactions, between phenol molecules or ions and the A-BC surface compared to the interactions among phenol molecules or ions in solution, resulting in the release of energy during the adsorption process.

3.7 Adsorption mechanism

Based on the experimental results, we conclude that the adsorption of phenol on A-BC is the result of various mechanisms such as physical adsorption, chemical adsorption, and electrostatic attraction. A-BC's large specific surface area and well-developed micro-mesoporous structure facilitate multilayer adsorption of phenol onto A-BC, this is consistent with the experimental results of Shen and Fu [63], accompanied by chemical adsorption [64]. FT-IR analysis indicates that functional groups such as -OH, C=O, N-H, and C-O-C on A-BC are involved in phenol adsorption [65]. -OH groups can adsorb phenol molecules through hydrogen bonding, while N-H, C–O–C, and C=O groups facilitate phenol adsorption by providing π -electron donor sites and hydrogen bonding [66]. In addition, the hydroxyl group in phenol exhibits a p- π conjugation effect with the benzene ring, which enhances the interaction between phenol and biochar, thereby facilitating the adsorption of phenol onto A-BC **[63]**.

3.8 Reusability of A-BC

An aliquot of 0.02 g of A-BC, washed and eluted with distilled water, was reintroduced into a 20 mL solution containing 400 mg L⁻¹ of phenol, and subjected to agitation for 60 min in five repeated adsorption-desorption experiments (Fig. 12). This demonstrated that after washing and elution with distilled water, A-BC retained a significant adsorption capacity over five repeated uses. The adsorption capacity for phenol decreased from 161 to 120 mg g^{-1} , maintaining 75% of its initial adsorption capacity, indicating good stability and recyclability of A-BC. Studies have shown that using nitric acid, hydrochloric acid, ethylenediaminetetraacetic acid, and sodium hydroxide as elution solvents for biochar result in better regeneration effects, but may generate waste salts requiring further treatment [67, 68]. To avoid secondary structural changes and waste salt formation, distilled water was used as the elution agent for the recycled A-BC in this experiment. The decrease in phenol adsorption capacity upon repeated use of A-BC may be attributed to distilled water effectively washing off phenol adsorbed



Fig. 12 Reusability performance of A-BC in adsorbing phenol. Experimental conditions: dosage of A-BC, 1.0 g L⁻¹; initial phenol concentration, 400 mg L⁻¹; initial pH of solution unadjusted; contact time, 0–360 min; solution volume, 20 mL; temperature, 25 °C

Table 6 Measurement results of actual water samples. Experimental conditions: dosage of A-BC, 1.0 g L⁻¹; initial phenol concentration, 675 mg L⁻¹; initial pH of solution unadjusted; contact time, 60 min; solution volume, 20 mL; temperature, 25 °C

Actual water	Sample ID	1	2	3	4	5	6	
	$Q_e (mg g^{-1})$	150	149	149	149	149	149	
	Mean	149 mg g	$149 \mathrm{mg g}^{-1}$					
	Absolute deviation	0.23	-0.30	-0.06	0.19	-0.09	0.05	
	Relative mean deviation (%)	0.10						
Simulated wastewater	$Q_e (mg g^{-1})$	161						
Relative error between actual	water samples and simulated waste	water (%)		-7.46				

on the surface but only partially removing phenol inside the pores. Additionally, phenol molecules or ions washed off from the A-BC surface may lead to deactivation or reduced activity of corresponding adsorption sites, thereby limiting phenol re-adsorption.

3.9 Adsorption of actual water samples by A-BC

Following the procedures outlined in Sect. 2.4.5, six actual water samples (with water quality indicators detailed in Sect. 2.1) were subjected to A-BC adsorption experiments. The results are presented in Table 6. Table 6 shows that the average adsorption capacity of phenol by A-BC in the six actual water samples was 149 mg g⁻¹, which is 7.5% lower than the 161 mg g⁻¹ observed in simulated water samples. This suggests that A-BC has promising applications in the adsorption of phenol-containing wastewater from coal chemical industries. The lower adsorption capacity of phenol from actual water samples

compared to simulated ones may be related to the low adsorption selectivity of biochar. Wastewater generated by coal chemical enterprises contains other phenolic compounds, ammonia nitrogen, and other organic substances, which can compete with phenol for adsorption sites on A-BC.

4 Conclusions

In this study, A-BC was prepared by jointly modifying biochar with KOH and EDTA-4Na for the purpose of adsorbing phenol in aqueous solutions. At 25 °C, A-BC exhibited equilibrium adsorption capacities of 161 mg g^{-1} for simulated water samples and 149 mg g^{-1} for coal chemical wastewater samples, significantly higher than unmodified biochar The well-developed pore structure of A-BC lays a solid foundation for phenol adsorption, while the abundant functional groups provide conditions for A-BC to chemically adsorb phenol through hydrogen bonding and π - π interactions. The good thermal stability and amorphous graphite structure of A-BC make it possible for repeated use. A-BC exhibits strong adsorption capacity for phenol, good stability, and can be reused, offering a simple and efficient strategy for removing phenol from wastewater in coal chemical enterprises as well as other water bodies. The preparation process of A-BC obtained in this experiment is simple and has certain application prospects in the treatment of organic wastewater containing phenol, such as coal chemical, petrochemical, coking, pharmaceutical, and printing and dyeing industries. The data and results obtained in this experiment can provide theoretical and empirical support for the development of green, economical, and efficient adsorbents.

Acknowledgements

The authors are grateful to Xinjiang Agricultural University, China.

Authors' contributions

Yanqin Chen: Writing – review & editing, Conceptualization, Methodology, Funding Acquisition; Donghui Wang: Experiment, Formal analysis, Software, Resources, Visualization; Xueli Wang: Experiment, Investigation, Formal Analysis and mining, Writing – original draft, Supervision; Jing Wu: Experiment, Data curation. Shifang Song: Validation, Data curation, Project Administration.

Funding

This work was supported by the National Natural Science Foundation of China (Grant No. 21066013).

Data availability

All relevant data are included in the paper or its Supplementary Information.

Declarations

Competing interests

The authors declare they have no competing interests.

Received: 29 July 2024 Accepted: 3 February 2025 Published online: 18 February 2025

References

- Michalowicz J, Duda W. Phenols-sources and toxicity. Pol J Environ Stud. 2007;16:347–62.
- Xu Y, Bai T, Yan Y, Zhao Y, Yuan L, Pan P, et al. Enhanced removal of hexavalent chromium by different acid-modified biochar derived from corn straw: behavior and mechanism. Water Sci Technol. 2020;81:2270–80.
- Yang L, Liu Y, Zhang A, Liu Z, Yang Z, Li X, et al. Construction of aldehydebased, ester-based hyper-cross-linked polar resin and its selective adsorption mechanism for phenol in coal chemical wastewater. Environ Res. 2024;246:118140.
- Gao W, Lin Z, Chen H, Yan S, Zhu H, Zhang H, et al. Roles of graphitization degree and surface functional groups of N-doped activated biochar for phenol adsorption. J Anal Appl Pyrol. 2022;167:105700.
- Zhao C, Lin X, Su X, Zhang S. Efficient degradation of phenol in water by ball-milling modulated nitrogen-doped structured biochar. J Environ Chem Eng. 2024;12:112397.

- Zhang L, Li B, Shao P, Zhou X, Li D, Hu Z, et al. Selective capture of palladium from acid wastewater by thiazole-modified activated carbon: Performance and mechanism. Environ Res. 2023;238:117253.
- Aborisade MA, Feng A, Zheng X, Oba BT, Kumar A, Battamo AY, et al. Carbothermal reduction synthesis of eggshell-biochar modified with nanoscale zerovalent iron/activated carbon for remediation of soil polluted with lead and cadmium. Environ Nanotechnol Monit Manag. 2022;18:100726.
- Aborisade MA, Oba BT, Kumar A, Liu J, Chen D, Okimiji OP, et al. Remediation of metal toxicity and alleviation of toxic metals-induced oxidative stress in Brassica chinensis L using biochar-iron nanocomposites. Plant Soil. 2023;493:629–45.
- Aborisade MA, Feng A, Oba BT, Kumar A, Battamo AY, Huang M, et al. Pyrolytic synthesis and performance efficacy comparison of biocharsupported nanoscale zero-valent iron on soil polluted with toxic metals. Arch Agron Soil Sci. 2023;69:2249–66.
- Lee KS, Park MS, Kim JD. Nitrogen doped activated carbon with nickel oxide for high specific capacitance as supercapacitor electrodes. Colloid Surface A. 2017;533:323–9.
- Burchacka E, Lukaszewicz M, Kulazynski M. Determination of mechanisms of action of active carbons as a feed additive. Bioorg Chem. 2019;93:102804.
- 12. Alam MG, Danish M, Alanazi AM, Ahmad T, Khalil HPSA. Response surface methodology approach of phenol removal study using high-quality activated carbon derived from H_3PO_4 activation of *Acacia mangium* wood. Diam Relat Mater. 2023;132:109632.
- 13. El-Bery HM, Saleh M, El-Gendy RA, Saleh MR, Thabet SM. High adsorption capacity of phenol and methylene blue using activated carbon derived from lignocellulosic agriculture wastes. Sci Rep. 2022;12:5499.
- Makvandi F, Alijani H, Taghavi M, Rastegarzadeh S. High-performance removal of phenol from aqueous solutions using EG- and PEG-functionalized biochar: equilibrium, kinetic and thermodynamic study with optimization by response surface methodology (RSM). Res Chem Intermediat. 2023;49:1601–28.
- Dehmani Y, Lamhasni T, Mohsine A, Tahri Y, Lee HS, Lgaz H, et al. Adsorption removal of phenol by oak wood charcoal activated carbon. Biomass Convers Bior. 2024;14:8015–27.
- da Silva MCF, Schnorr C, Lutke SF, Knani S, Nascimento VX, Lima EC, et al. KOH activated carbons from Brazil nut shell: Preparation, characterization, and their application in phenol adsorption. Chem Eng Res Des. 2022;187:387–96.
- Nabais JMV, Laguinhas CE, Roman S. Biomass novel adsorbents for phenol and mercury removal. Molecules. 2022;27:7345.
- Zhang X, Shu X, Zhou X, Zhou C, Yang P, Diao M, et al. Magnetic reed biochar materials as adsorbents for aqueous copper and phenol removal. Environ Sci Pollut R. 2023;30:3659–67.
- Li M, Wang Y, Liu Y, Wang H, Song H. Preparation of active carbon through one-step NaOH activation of coconut shell biomass for phenolic wastewater treatment. Res Chem Intermediat. 2022;48:1665–84.
- Nwabanne JT, Iheanacho OC, Obi CC, Onu CE. Linear and nonlinear kinetics analysis and adsorption characteristics of packed bed column for phenol removal using rice husk-activated carbon. Appl Water Sci. 2022;12:91.
- Kumar A, Rout DR, Jena HM. Phosphoric acid modified activated carbon prepared from Fox nutshell for adsorption of phenol: batch and continuous studies. Int J Environ an Ch. 2024;104:6979–96.
- Li H, Zhang J, Li F, Luo S, Li Q, Zhou S. Preparation of waste coffee grounds carbon and study on phenol adsorption ability. J Wuhan Univ Technol. 2022;37:38–46.
- 23. Wei X, Huang S, Yang J, Liu P, Li X, Wu Y, et al. Adsorption of phenol from aqueous solution on activated carbons prepared from antibiotic mycelial residues and traditional biomass. Fuel Process Technol. 2023;242:107663.
- Zhou Y, Zhang X, Deng J, Li C, Sun K, Luo X, et al. Adsorption and mechanism study for phenol removal by 10% CO₂ activated bio-char after acid or alkali pretreatment. J Environ Manage. 2023;348:119317.

- 25. Melo JM, Lutke SF, Igansi AV, Franco DSP, Vicenti JRM, Dotto GL, et al. Mass transfer and equilibrium modelings of phenol adsorption on activated carbon from olive stone. Colloids Surfaces A. 2024;680:132628.
- Li M, Mu J, Liu Y, Wang H, Wang Y, Song H. Removal of phenol by ligninbased activated carbon as an efficient adsorbent for adsorption of phenolic wastewater. Res Chem Intermediat. 2023;49:2209–32.
- Dehmani Y, Franco DSP, Georgin J, Lamhasni T, Brahmi Y, Oukhrib R, et al. Towards experimental and theoretical understanding of the adsorption behavior of phenol on a new activated carbon prepared from oak wood. J Water Process Eng. 2023;54:103936.
- Ma J, Ankit G, Zhong F, Li C, Liu N, Niu W, et al. Coupling behavior and enhancement mechanism of porous structure, graphite microcrystals, and oxygen-containing groups of activated biochar for the adsorption of phenol. Environ Sci Wat Res. 2023;9:1944–57.
- Pei T, Shi F, Hou D, Yang F, Lu Y, Liu C, et al. Enhanced adsorption of phenol from aqueous solution by KOH combined Fe-Zn bimetallic oxide copyrolysis biochar: Fabrication, performance, and mechanism. Bioresource Technol. 2023;388:129746.
- Pei T, Shi F, Liu C, Lu Y, Lin X, Hou D, et al. Bamboo-derived nitrogendoping magnetic porous hydrochar coactivated by K₂FeO₄ and CaCO₃ for phenol removal: Governing factors and mechanisms. Environ Pollut. 2023;331:121871.
- Qu J, Du Z, Lei Y, Li M, Peng W, Wang M, et al. Microwave-assisted one-pot preparation of magnetic cactus-derived hydrochar for efficient removal of lead(II) and phenol from water: Performance and mechanism exploration. Bioresource Technol. 2023;388:129789.
- Oyehan TA, Azeez MO, Abdulazeez I, Yusuf BO, Ganiyu SA, Jamiu ZA, et al. Experimental and DFT investigation of phenol adsorption onto cobalt nanoparticles-modified porous carbon. Arab J Sci Eng. 2024;49:547–63.
- An Q, Chen D, Tang Y, Hu Y, Feng Y, Qian K, et al. Adsorption of pyrolysis oil model compound (phenol) with plasma-modified hydro-chars and mechanism exploration. Environ Sci Pollut R. 2023;30:122611–24.
- da Silva MCF, Lutke SF, Nascimento VX, Lima EC, Silva LFO, Oliveira MLS, et al. Activated carbon prepared from Brazil nut shells towards phenol removal from aqueous solutions. Environ Sci Pollut R. 2023;30:82795–806.
- 35. Arumugham T, Yuniarto A, Abdullah N, Yuzir A, Kamyab H, Pa NFC, et al. Preparation and characterisation of porous activated carbon using potassium hydroxide chemical activation with ultrasonic association. Biomass Convers Bior. 2023. in press.
- Obanla OR, Hestekin JA, Ojewumi ME, Bousrih I, Fawole MC. Enhancing rubber (*Hevea brasiliensis*) seed shell biochar through acid-base modification for effective phenol removal from aqueous environments. Results Eng. 2023;20:101584.
- Abdulrahman MS, Alsarayreh AA, Barno SKA, Elkawi MAA, Abbas AS. Activated carbon from sugarcane as an efficient adsorbent for phenol from petroleum refinery wastewater: Equilibrium, kinetic, and thermodynamic study. Open Eng. 2023;13:20220442.
- Darla UR, Lataye DH, Kumar A, Pandit B, Ubaidullah M. Adsorption of phenol using adsorbent derived from Saccharum officinarum biomass: optimization, isotherms, kinetics, and thermodynamic study. Sci Rep. 2023;13:18356.
- Mesquita MdS, Tanabe EH, Bertuol DA. Adsorption of phenol using Eucalyptus saligna biochar activated with NiCl₂. Water Air Soil Poll. 2024;235:311.
- Cao P, Li Y, Shao J. Experimental study on the preparation of ligninbased activated carbon and its adsorption performance for phenol. ACS Omega. 2024;9:24453–63.
- Long⁻⁷, Wen J, Xu B, Zeng L, Zhu L, Xiao M, et al. Reusable biochars derived from *Camellia oleifera* shell via K₂CO₃ activated for phenolenhanced adsorption. Ind Crop Prod. 2024;220:119263.
- Liu L, Shi S, Hu H, Huang Y. Investigation of phenol adsorption performance and mechanism using Na₂EDTA-modified activated biochars produced from a fluidized bed pyrolysis system. Biomass Bioenerg. 2024;183:107164.
- 43. Lingamdinne LP, Angaru GKR, Pal CA, Koduru JR, Karri RR, Mubarak NM, et al. Insights into kinetics, thermodynamics, and mechanisms of chemically activated sunflower stem biochar for removal of phenol and bisphenol-A from wastewater. Sci Rep. 2024;14:4267.

- Zhang Y, Xu J, Li B, Xie Z, Li X, Tang J, et al. Enhanced adsorption performance of tetracycline in aqueous solutions by KOH-modified peanut shell-derived biochar. Biomass Convers Bior. 2023;13:15917–31.
- Lv S, Li C, Mi J, Meng H. A functional activated carbon for efficient adsorption of phenol derived from pyrolysis of rice husk, KOH-activation and EDTA-4Na-modification. Appl Surf Sci. 2020;510:145425.
- 46. Encinas-Vazquez A, Quezada-Renteria JA, Cervantes FJ, Perez-Rabago CA, Molina-Freaner FE, Pat-Espadas AM, et al. Unraveling the mechanisms of lead adsorption and ageing process on high-temperature biochar. J Chem Technol Biot. 2021;96:775–84.
- 47. Alves BSQ, Fernandes LA, Southard RJ. Biochar-cadmium retention and its effects after aging with hydrogen peroxide (H_2O_2). Heliyon. 2021;7:e08476.
- Maaloul N, Oulego P, Rendueles M, Ghorbal A, Diaz M. Novel biosorbents from almond shells: Characterization and adsorption properties modeling for Cu(II) ions from aqueous solutions. J Environ Chem Eng. 2017;5:2944–54.
- Wang X, Chen Y, Song S. Optimization of preparation process of almond shell biochar by response surface methodology. Chem Eng-China. 2023;51:33–8 [in Chinese]. https://imiy.chinajournal.net.cn/WKB2/WebPu blication/paperDigest.aspx?paperID=d5535a27-23ac-4df6-b9b2-336ba dca778a# (Accessed 30 Dec 2024)
- Jin R, Zhao C, Song Y, Qiu X, Li C, Zhao Y. Competitive adsorption of sulfamethoxazole and bisphenol A on magnetic biochar: Mechanism and site energy distribution. Environ Pollut. 2023;329:121662.
- Zhang H, Li R, Zhang Z. A versatile EDTA and chitosan bi-functionalized magnetic bamboo biochar for simultaneous removal of methyl orange and heavy metals from complex wastewater. Environ Pollut. 2022;293:118517.
- Kumar NS, Shaikh HM, Asif M, Al-Ghurabi EH. Engineered biochar from wood apple shell waste for high-efficient removal of toxic phenolic compounds in wastewater. Sci Rep. 2021;11:2586.
- 53. Liu Y, Niu MS, Yi X, Li G, Zhou H, Gao W. Boron vacancies of mesoporous MnO₂ with strong acid sites, free Mn³⁺ species and macropore decoration for efficiently decontaminating organic and heavy metal pollutants in black-odorous waterbodies. Appl Surf Sci. 2021;561:150081.
- Li R, Wang Z, Guo J, Li Y, Zhang H, Zhu J, et al. Enhanced adsorption of ciprofloxacin by KOH modified biochar derived from potato stems and leaves. Water Sci Technol. 2018;77:1127–36.
- 55. Yan S, Chu S, Xu H, Zhu H, Chen H, Gao W, et al. Study on adsorption performance of biochar with different particle size on phenol and bio-oil. J For Eng. 2023;4:95–101 [in Chinese]. http://lygcxb.njfu.edu.cn/#/digest? ArticleID=4887 (Accessed 30 Dec 2024)
- Masoumi S, Dalai AK. Optimized production and characterization of highly porous activated carbon from algal-derived hydrochar. J Clean Prod. 2020;263:121427.
- Feng D, Guo D, Zhang Y, Sun S, Zhao Y, Shang Q, et al. Functionalized construction of biochar with hierarchical pore structures and surface O-/Ncontaining groups for phenol adsorption. Chem Eng J. 2021;410:127707.
- Stavropoulos GG, Samaras P, Sakellaropoulos GP. Effect of activated carbons modification on porosity, surface structure and phenol adsorption. J Hazard Mater. 2008;151:414–21.
- Franco DSP, Georgin J, Netto MS, Allasia D, Oliveira MLS, Foletto EL, et al. Highly effective adsorption of synthetic phenol effluent by a novel activated carbon prepared from fruit wastes of the *Ceiba speciosa* forest species. J Environ Chem Eng. 2021;9:105927.
- Song M, Song B, Meng F, Chen D, Sun F, Wei Y. Incorporation of humic acid into biomass derived carbon for enhanced adsorption of phenol. Sci Rep. 2019;9:19931.
- Allahkarami E, Dehghan Monfared A, Silva LFO, Dotto GL. Toward a mechanistic understanding of adsorption behavior of phenol onto a novel activated carbon composite. Sci Rep. 2023;13:167.
- Qu Y, Qin L, Liu X, Yang Y. Magnetic Fe₃O₄/ZIF-8 composite as an effective and recyclable adsorbent for phenol adsorption from wastewater. Sep Purif Technol. 2022;294:121169.
- Shen Y, Fu Y. KOH-activated rice husk char via CO₂ pyrolysis for phenol adsorption. Mater Today Energy. 2018;9:397–405.
- Dąbrowski A, Podkościelny P, Hubicki Z, Barczak M. Adsorption of phenolic compounds by activated carbon—a critical review. Chemosphere. 2005;58:1049–70.

- 65. Li Z, Sun Y, Yang Y, Han Y, Wang T, Chen J, et al. Biochar-supported nanoscale zero-valent iron as an efficient catalyst for organic degradation in groundwater. J Hazard Mater. 2020;383:121240.
- Zong P, Cheng Y, Wang S, Wang L. Simultaneous removal of Cd(II) and phenol pollutions through magnetic graphene oxide nanocomposites coated polyaniline using low temperature plasma technique. Int J Hydrogen Energ. 2020;45:20106–19.
- Jiang S, Yan L, Wang R, Li G, Rao P, Ju M, et al. Recyclable nitrogen-doped biochar via low-temperature pyrolysis for enhanced lead(II) removal. Chemosphere. 2022;286:131666.
- Xin O, Yitong H, Xi C, Jiawei C. Magnetic biochar combining adsorption and separation recycle for removal of chromium in aqueous solution. Water Sci Technol. 2017;75:1177–84.

Publisher's Note

Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.