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Enhanced Cd²⁺ Adsorption by Na₂SeO₃-Modified Grapevine Pruning Waste-Derived Biochar (Se-GBC):

Synthesis, Characterization, and Mechanism

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Abstract

The utilization rate of grapevine pruning waste for resource recovery is low, with most material being disposed of through incineration, creating an urgent need for high-value transformation. To develop an adsorbent with high Cd^{2+} adsorption performance, three types of grape pruning waste-derived biochar (GBC) were prepared at relatively low pyrolysis temperatures (300, 400, and 500°C) and modified by loading different proportions of trace Na_2SeO_3 ; the mechanisms underlying Cd^{2+} adsorption were further investigated. The results indicate that Cd^{2+} adsorption onto GBC follows a monolayer adsorption model involving both physical and chemical processes. Among the samples, GBC pyrolyzed at 400°C, and modified at a Se: GBC mass ratio of 1:1500, exhibited the highest efficiency, showing a 61.03% increase in adsorption capacity compared to the unmodified biochar. The loading of Na_2SeO_3 increased the proportion of oxygen-containing functional groups (OFGs) such as C-O, C=O, and -COOH, on the GBC surface, thereby enhancing complexation and ion exchange with Cd^{2+} , promoting the formation of insoluble precipitates and effectively immobilize Cd^{2+} . These findings provide a scientific basis for the resource utilization of grapevine pruning waste in heavy metal remediation and clarify the adsorption mechanism of Se-GBC for Cd^{2+} .

Keywords: Grapevine pruning waste-derived biochar, Selenium-modification, Cadmium, Adsorption mechanism

Statements and Declarations

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Introduction

The rapid development of the table grape and wine industries has led to a continuous expansion of grape cultivation areas. Statistics indicate that China's grape cultivation area reached 10.5657 million *mu* (approximately 704,380 *hectares*) in 2022, ranking second in the world (Sun *et al.*, 2020). Concurrently, the global annual production of grapevine pruning waste from vineyard management exceeds 4200 tons (Wong *et al.*, 2020), making its resource recovery an important contemporary environmental issue. Traditional disposal methods for grapevine pruning residues-such as leaving them in fields, burning them, or discarding them indiscriminately-cause environmental pollution by increasing pest and disease risks, releasing PM_{2.5} particles (Chen *et al.*, 2022), and occupying valuable farmland. Consequently, the resource utilization rate of grapevine pruning waste remains persistently low (Zhu *et al.*, 2024). Therefore, developing high-value utilization technologies for this waste stream is crucial for promoting sustainable agriculture and improving environmental protection.

The emergence of pyrolysis technology has provided a new pathway for valorizing agricultural and forestry by-products. Pyrolysis is an oxygen-limited thermochemical process that converts biomass into biochar (BC), along with gaseous and liquid products. BC is characterized by a elevated specific surface area, hierarchically organized porosity, and diversified surface functionality (Lan *et al.*, 2024). Due to these properties, BC has been widely applied in heavy metal remediation, especially for the efficient removal of Cd²⁺. Grapevine pruning waste, with high lignin content, rich micronutrients (e.g., K, Ca, Mg, etc.) (Ibn Ferjani *et al.*, 2019), and a natural fibrous structure that facilitates pore formation during pyrolysis, is a promising raw material for biochar production. Its internal fibrous structure facilitates the formation of natural pores during pyrolysis. The combination of a porous structure and alkaline mineral

composition makes it a suitable material for heavy metal remediation. For instance, BC derived from grape pruning waste has demonstrated an adsorption capacity of 5.73 mg/g for polyphenolic compounds (Prelac *et al.*, 2023) and up to 156.12 mg/g for Lead (Pb) in water (Li *et al.*, 2018). Consequently, grapevine pruning waste is also likely to exhibit strong potential for adsorbing Cd²⁺. In a related study, (Hamzenejad Taghlidabad & Sepehr, 2018) observed that after applying BC from grapevine branches, the exchangeable cadmium content in soil decreased by 0.4 mg/kg, and the carbonate-bound cadmium content was reduced by 1.9 mg/kg. The properties of BC are influenced by factors including feedstock type, pyrolysis temperature, and heating rate, with the biomass feedstock playing a particularly significant role (Yang *et al.*, 2020). However, the adsorption sites within the pore structure of pristine BC are inherently limited (Zhang *et al.*, 2023), which constrains its Cd²⁺ adsorption capacity. Therefore, post-synthesis modification is commonly employed to enhance adsorption performance through methods such as ball milling, chitosan coating, and chemical activation (e.g., with NaOH or HNO₃) (Lan *et al.*, 2024). The pore structure of GBC is inherently constrained by its raw material architecture, often resulting in high ash content and a limited variety of functional groups. Therefore, modifying GBC remains a necessary step to improve its environmental remediation performance. While extensive research exists on Cd²⁺ adsorption by modified biochar in general, studies specifically investigating the enhancement mechanisms for GBC remain relatively limited.

Selenium (Se), an essential trace element, exhibits antagonistic effects against heavy metals (Huang *et al.*, 2021; Zhang *et al.*, 2020). and Se-modified biochar can enhance Cd²⁺ immobilization in soil and water by increasing the number of OFGs and improving hydrophilicity (Wang *et al.*, 2025). Grape pruning waste has been proven feasible for biochar production via pyrolysis and its inherent alkaline mineral composition and porous structure make it a suitable substrate for Se modification, which can

combine the advantages of selenium's heavy metal antagonism and biochar's adsorption performance (Beigmohammadi *et al.*, 2024; Dorosh *et al.*, 2025). However, existing studies have not explored the Se modification of GBC, and the adsorption efficacy and underlying mechanisms of Se-modified GBC for Cd^{2+} remain unclear. Moreover, most current studies focus on high-temperature pyrolysis ($>500^{\circ}\text{C}$) for GBC preparation, with limited research on low-temperature pyrolysis and the optimization of selenium modification ratios.

Aiming at the above research gaps, this study prepared BCs from grape pruning waste via low-temperature pyrolysis ($300\text{--}500^{\circ}\text{C}$) and modified them with different proportions of Na_2SeO_3 . The specific research objectives were set as follows: (1) to examine the effect of relatively low pyrolysis temperatures ($300^{\circ}\text{C}\text{--}500^{\circ}\text{C}$) on the properties of GBC; (2) to evaluate the impact of Na_2SeO_3 dosage on the characteristics and Cd^{2+} adsorption performance of GBC; and (3) to elucidate the adsorption mechanisms of the modified GBC for Cd^{2+} via kinetic and adsorption isotherm analyses combined with multi-characterization techniques.

2 Materials and Methods

2.1 Materials

Grapevine pruning waste was collected from a vineyard in Honggu District, Lanzhou, Gansu Province ($36^{\circ}14'27''\text{N}$, $103^{\circ}5'57''\text{E}$). The vineyard was planted with the cultivar 'Tiangong Moyu'. After removing impurities such as withered leaves and soil, the prunings were air-dried under shaded and ventilated conditions for approximately three months to reduce moisture content. The dried material was then cut into segments approximately 40 cm in length and stored for further use. Cd^{2+} was supplied in the form of cadmium sulfate octahydrate ($\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$), and Se was sourced from sodium selenite (Na_2SeO_3). All solutions were prepared using distilled water, and the pH was adjusted with 0.1 M NaOH

or 0.1 M HCl as required.

2.2 Preparation and Modification of GBC

Approximately 20 kg of grapevine prunings were loaded into a pyrolysis furnace under an oxygen-limited atmosphere. The temperature was raised to the target levels (300, 400, and 500°C) at a heating rate of 10°C/min and maintained for 2 h after reaching each target temperature. Following pyrolysis, the furnace was cooled to below 50°C before the GBCs were collected. The resulting GBC was ground and sieved through a 100-mesh screen, and the raw GBC produced at the different pyrolysis temperatures were designated as GBC300, GBC400, and GBC500, respectively.

For modification, a predetermined mass of Na₂SeO₃ was dissolved in 20 mL of distilled water and mixed with GBC powder at Se: GBC mass ratios of 1:500, 1:1000, 1:1500, and 1:2000. The mixture was oscillated at 25°C and 250 rpm for 24 h, then dried at 70°C to a constant weight and stored for further use.

The adsorption experiments and characterizations are described in the supplementary materials.

3. Results and Discussion

3.1 Specific surface area and pore structure

Pyrolysis temperature significantly altered the pore structure and specific surface area of GBCs (Yang *et al.*, 2021). As shown in Table S1, the specific surface area of GBCs increased from 10.07 m²/g to 76.67 m²/g with rising pyrolysis temperature, primarily due to the disruption of the biomass's inherent lignocellulosic structure and the release of volatile matter, which creates new pores. The magnitude of the specific surface area plays a pivotal role in dictating the adsorption capacity. Previous studies align with this trend. For instance, Zhang *et al.* reported that as pyrolysis temperature increased from 300°C to 700°C, the specific surface area of mango seed biochar rose from 0.96 m²/g to 5.58 m²/g, with a

corresponding increase in pore volume (Zhang et al., 2023). However, the pore volume of GBC exhibited a notable decline at 500°C (5×10^{-4} cm³/g), compared to 300°C (2.9×10^{-3} cm³/g) with the average pore diameter also decreasing continuously. This is because high temperatures promote the formation of small-diameter micropores (increasing surface area) but also cause thermal collapse and coalescence of mesopores, leading to a sharp reduction in total pore volume and poor mass transfer efficiency for Cd²⁺.

After modification with Na₂SeO₃, the specific surface area (38.81 m²/g) and pore volume (5.3×10^{-3} cm³/g) of Se-GBC400 slightly decreased compared to GBC400, while the average pore diameter increased significantly to 54.47 nm (Table S1). The slight reduction in surface area and pore volume is attributed to the partial blockage of pore channels by Na₂SeO₃ particles or their decomposition products, a phenomenon consistent with other modified biochar systems (Li *et al.*, 2023). Notably, the significant increase in average pore diameter effectively compensates for the loss of surface area: the macroporous structure (>50 nm) of Se-GBC400 greatly reduces the diffusion resistance of Cd²⁺ ions, facilitating their rapid transport from the solution to the internal active sites of the biochar, which is a key structural factor for the improved adsorption performance of Se-GBC400; this structural characteristic is also supported by the N₂ adsorption-desorption isotherm results (Fig. S2) and SEM characterization (Fig. 1d).

The SEM images of GBCs were shown in Fig. 1. Unmodified GBC exhibits an irregular, honeycomb-like structure, a typical characteristic of pyrolyzed lignocellulosic biomass resulting from the removal of volatile compounds (Wang *et al.*, 2021). As the pyrolysis temperature increased, the cracking and rearrangement of lignin and cellulose components led to structural shrinkage, transforming the GBCs surface from relatively smooth (GBC300) to more textured and rough (GBC400, GBC500). In contrast to studies where modifiers form distinct surface nanoparticles, the surface morphology of Se-GBC400 (Fig.1d) showed no visually significant difference from that of GBC400. This is attributed to

the low loading amount of Na_2SeO_3 (1:1500) and its potential integration into the biochar matrix or pore walls without forming large, discrete particulate deposits (Deng *et al.*, 2021), which ensures that the active sites introduced by modification are evenly distributed on the biochar surface and inside the pores.

The N_2 adsorption-desorption isotherms revealed the pore characteristics of the biochars (Fig. S2). The isotherms for GBC400, GBC500, and Se-GBC400 were all classified as Type IV with H3-type hysteresis loops (IUPAC classification) (Thommes *et al.*, 2015), characteristic of materials containing slit-shaped pores and macropores while the isotherm for GBC300 did not conform to this type. After modification, the pore size distribution of Se-GBC400 showed an increased proportion in the macropore range (> 50 nm), which is consistent with the increased average pore diameter (Table S1) and further confirmed that Se modification optimizes the pore structure of GBC400 for Cd^{2+} diffusion.

3.2 Characteristics of the original GBCs and Se-GBC400

3.2.1 XRD Analysis

The XRD patterns of unmodified GBCs and Se-GBC400 were shown in Fig. 2a. The unmodified GBCs exhibited broad diffraction peaks at lower angles (approximately $20\text{--}30^\circ$ 2θ), indicative of a predominantly amorphous carbon structure, which provides a large number of aromatic ring structures for Cd^{2+} adsorption via π -Cd interactions. Distinct diffraction peaks were observed at $2\theta = 29.4^\circ$, 39.5° , and 34.2° , corresponding to crystalline calcium carbonate (CaCO_3 ; PDF# 99-0022), the primary crystalline phase of GBC, and the intensity of these CaCO_3 peaks increased with rising pyrolysis temperature, which is consistent with the increasing alkalinity of GBC (Table S1) (Qi *et al.*, 2025).

Following the modification of GBC400 to produce Se-GBC400, the broad diffraction signal of amorphous carbon was retained (ensuring the basic aromatic structure for adsorption), and new diffraction peaks at $2\theta = 30.34^\circ$, 32.54° , and 35.98° were observed, corresponding to the crystalline

phases of calcium selenide (CaSe; PDF# 18-0304) and selenium dioxide (SeO₂; PDF# 22-1314). This demonstrates that Se not only remained in an ionic state on the GBC surface but also reacted with the inorganic components (e.g., CaCO₃) of biochar to form distinct Se-containing crystalline compounds. The formation of CaSe and SeO₂ not only increases the crystallinity of Se-GBC400 but also introduces a large number of Se-O functional groups on the biochar surface, which can provide additional active sites for Cd²⁺ complexation and precipitation, thus directly enhancing the chemical adsorption capacity of Se-GBC400 for Cd²⁺.

3.2.2 FTIR Analysis

FTIR spectrometry of GBCs before and after modification was performed in the wavelength range of 400-4000 cm⁻¹ (Fig. 2b). The overall profile of functional groups was similar before and after modification, but notable changes in band intensities were observed, which directly reflect the variation of surface functional groups and their contribution to Cd²⁺ adsorption.

For the unmodified GBC, as the pyrolysis temperature increased from 300°C to 500°C, the stretching vibration intensities of -OH (~3435 cm⁻¹), C=C (~1622 cm⁻¹), and C-O (~1141 cm⁻¹) (Fan *et al.*, 2025; Zhang *et al.*, 2025), while the intensity of C-H stretching bands (~1419 cm⁻¹ and 870 cm⁻¹) was enhanced. This reduction in oxygen-containing functional groups is primarily attributed to dehydration, decarboxylation, and dehydroxylation reactions at high temperatures, and the increase in C-H bands indicates the enhanced aromaticity of GBC (Mei *et al.*, 2021); This trend is consistent with the elemental analysis results (Table S1) of decreasing O content and increasing C content with rising temperature, and also explains the limited Cd²⁺ adsorption capacity of high-temperature pyrolyzed GBC500 despite its large specific surface area.

Compared to GBC400, the spectrum of Se-GBC400 showed enhanced intensity for the bands corresponding to -OH ($\sim 3435\text{ cm}^{-1}$), C=C ($\sim 1622\text{ cm}^{-1}$), and C-H ($\sim 1419\text{ cm}^{-1}$), indicating that Na_2SeO_3 modification not only increases the content of hydroxyl groups (a key OFGs for Cd^{2+} complexation) but also further enhances the aromaticity of GBC400 (favorable for π -Cd interactions). Furthermore, distinct shifts and enhanced intensities were observed in the peaks around 874 cm^{-1} and 579 cm^{-1} , which suggest the formation of Se-O or Se-C bonds on the Se-GBC400 surface (Feng *et al.*, 2022). The FTIR results confirmed that Na_2SeO_3 modification enriched the surface functional groups of GBC400 (including -OH, C-O, Se-O, and aromatic C=C), and these functional groups provide abundant active sites for complexation, ion exchange and π -Cd interacting with Cd^{2+} , which is the core chemical reason for enhancing Cd^{2+} adsorption capacity of Se-GBC-400.

3.2.3 XPS spectra Analysis

The XPS survey spectra of GBCs before and after modification were shown in Fig. 2c. The spectra for unmodified GBC exhibited characteristic peaks at binding energies of approximately 285 eV(C1s), 532 eV(O1s), and 400 eV(N1s) (Velez *et al.*, 2025), with relative intensity follows the order C1s > O1s > N1s. Minor peaks corresponding to Ca2p, K2p, and Si2p are also visible, consistent with the inorganic ash components of the biochar. Notably, a distinct Se peak is absent from the survey spectrum of Se-GBC400, which is attributed to the surface-sensitive nature of XPS (typical analysis depth of 5-10 nm), and the trace amount of Na_2SeO_3 (1:1500) that may have been incorporated into the biochar matrix below the immediate surface layer or was below the detection limit (Yan *et al.*, 2024). Despite the absence of the Se peak, the relative signal intensities of C, O and N elements in the XPS survey spectrum changed significantly after modification, which can directly reflect the variation of surface functional groups of Se-GBC400. A comparison of the survey spectra indicates a decrease in the relative carbon signal and a

concurrent increase in the oxygen signal for Se-GBC400 compared to GBC400, which directly confirmed the shift suggests an enrichment of OFGs on the surface of the modified biochar, aligning with the bulk elemental analysis (Table S1).

To investigate the chemical bonding states in detail, high-resolution scans of the C 1s, O 1s, and N 1s regions were performed (Fig.3). The C 1s spectra for all samples (Fig. 3a, b) were fitted with three primary components: the dominant peak at ~284.80 eV is assigned to graphite/sp² C-C bonds; the peak at ~286.68 eV correspond to carbon singly bonded to oxygen (C-O, in hydroxyl and ether groups); and the peak at ~289.06 eV is attributed to carbonyl/carboxyl groups (O-C=O). The signals from potassium K2p_{3/2} (~293.05 eV) and K2p_{1/2} (~296.13 eV) are visible as a doublet on the high-binding-energy side of the C 1s region (Fig. 3e, f) (Liu *et al.*, 2020). The deconvoluted O 1s spectra (Fig. 3c, d) primarily consist of contributions from C=O (~531.5 eV) and C-O (~533.0 eV) bonds. The N 1s spectra (Fig. 3e, f) were fitted with components for pyridinic N (~398.5 eV), pyrrolic N (~400.1 eV), and oxidized N (N-O, ~402-403 eV) (Wu *et al.*, 2023). For the unmodified GBC, the high-resolution data show that with increasing pyrolysis temperature, the relative contribution of C=O groups decreases while C-O groups increase (Fig. 3a, c). This trend is attributed to decarboxylation reactions at higher temperatures. In contrast, the C 1s spectrum of Se-GBC400 (Fig. 3b) shows a marked increase in the C-O component area compared to GBC400, confirming the successful surface enrichment with OFGs through Na₂SeO₃ modification. Corresponding increases in oxygenated and nitrogenated species are also seen in the O 1s and N 1s spectra of Se-GBC400 (Fig. 3d, f). These XPS results demonstrate that modification with Na₂SeO₃ effectively enhanced the population of OFGs on the biochar surface. This chemical modification increases the material's polarity and hydrophilicity, providing more active sites for complexation and ion exchange.

Consequently, Se-GBC400 exhibits a superior capacity for Cd^{2+} adsorption compared to the unmodified biochars.

3.3 Adsorption Performance of Pristine and Modified GBC

3.3.1 Adsorption Kinetics

The adsorption kinetic behavior of GBCs before and after modification is shown in Fig. 4a. For all samples, the adsorption capacity increased rapidly during the initial stage, then gradually decelerated, and finally stabilized beyond 800 min (reaching equilibrium); Se-GBC400 exhibited the fastest adsorption rate and the highest equilibrium adsorption capacity among all tested biochars, which is directly related to its optimized pore structure (large average pore diameter) and enriched surface functional groups (OFGs and Se-O groups) as characterized in Sections 3.1 and 3.2.

The two-staged adsorption behavior (rapid initial adsorption followed by slow adsorption until equilibrium) is consistent with other modified biochars (Ma *et al.*, 2023).

During the initial rapid stage (0~800 min), Cd^{2+} adsorption primarily occurred on the external surface of Se-GBC400, facilitated by the abundance readily accessible active sites and OFGs (e.g., -OH) that possess available lone electron pairs for rapid binding via both physical adsorption and surface complexation; as the surface sites were gradually occupied, the adsorption rate slowed, and the process became dominated by more stable chemisorption (e.g., ion exchange, π -Cd interactions) with Cd^{2+} diffusing into the internal pores of the biochar (Zhang *et al.*, 2021). The superior fast-stage adsorption rate of Se-GBC400 is attributed to its macroporous structure (low diffusion resistance) and high density of surface active sites, while the high equilibrium adsorption capacity is the result of the synergistic effect of physical adsorption and multiple chemical adsorption mechanisms.

The kinetic data were fitted with PFO and PSO models. The correlation coefficients (R^2) for the PSO model (0.9589, 0.9703, 0.9819, and 0.9769 for GBC300, GBC400, GBC500 and Se-GBC400, respectively) were consistently higher than those for the PFO model (0.9230, 0.9444, 0.9722, and 0.9417) (Table S2). Furthermore, the equilibrium adsorption capacities (Q_e) predicted by the PSO model were closer to the experimentally measured values. These results indicated that the adsorption of Cd^{2+} onto GBCs (especially Se-GBC400) is predominantly governed by chemisorption, involving the sharing or exchange of electrons between the adsorbent and adsorbate (Huang *et al.*, 2022).

To further investigate the diffusion mechanisms and the rate-limiting steps, the experimental data were analyzed using the Intraparticle Diffusion Model (IPD) (Fig. 4b). The adsorption process can be divided into three distinct linear stages for all samples: (1) rapid surface diffusion (0~120 min), (2) slow internal diffusion (120~800 min), and (3) adsorption equilibrium (>800 min), with calculated rate constants following the order $K_{int1} > K_{int2} > K_{int3}$ (Table S3), a typical trend for adsorption processes (Zhou *et al.*, 2025). Notably, the fitted IPD plots do not pass through the origin, confirming that while intraparticle diffusion is involved, it is not the sole rate-controlling step; surface adsorption and boundary layer effects also influence the overall kinetics (Ma *et al.*, 2023). Se-GBC400 exhibited the highest rate constant in the rapid surface diffusion stage ($K_{int1}=2.7134$), significantly higher than unmodified GBS (GBC300:0.8534; GBC400:0.9586; GBC500:2.1805). which is direct evidence that Se modification enhances the surface adsorption rate of GBC400 for Cd^{2+} , consistent with the characterization results of enriched surface functional groups and optimized pore structure.

3.3.2 Adsorption Isotherms

The adsorption isotherm for Cd^{2+} on GBCs before and after modification were presented in Fig. 4c. The adsorption capacities of all GBCs samples increased with rising initial Cd^{2+} concentrations until

approaching saturation, with the order of maximum adsorption capacity determined as: Se-GBC400 (24.52 mg/g) > GBC500 (22.34 mg/g) > GBC400 (22.34 mg/g) > GBC300 (13.05 mg/g). This order is consistent with the structural and chemical characteristics of the samples: GBC500 has a large specific surface area (physical adsorption advantage) but limited functional groups; Se-GBC400 has a slightly reduced surface area but an optimized pore structure and enriched functional groups (synergistic advantage of physical and chemical adsorption), resulting in the highest adsorption capacity.

Based on the model fitting parameters (Table S4), the Langmuir model yields a higher R^2 value for Se-GBC400 (0.9935) than the Freundlich model (0.9332), indicating that the adsorption of Cd^{2+} onto Se-GBC400 follows monolayer adsorption behavior as the dominant mode, which is attributed to the relatively homogeneous distribution of adsorption sites on the Se-GBC400 surface (introduced by uniform Se modification). A similar isotherm pattern had also been reported for $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ co-modified fruit peel biochar (FM-BC) in a previous study (Yang *et al.*, 2022). In the Freundlich model, the $1/n$ value of Se-GBC400 (0.4472) is lower than those of unmodified GBCs (GBC300: 0.5109; GBC400: 0.5388; GBC500: 0.5425), which suggests that the modified biochar surface offers more favorable conditions for Cd^{2+} adsorption with lower heterogeneity. Combined with the kinetic results, the adsorption of Cd^{2+} onto Se-GBC400 is a monolayer chemisorption process with heterogeneous surface characteristics, involving both physical and chemical adsorption.

3.3.3 Effects of Solution pH on Cd^{2+} Adsorption

Solution pH is a critical factor influencing the adsorption behavior of Cd^{2+} by altering the biochar surface change and Cd^{2+} chemical form in solution (Fig. 5a). Under strongly acidic conditions (pH 2-4), the adsorption capacity of all samples are low, with Se-GBC400 still exhibiting superior performance compared to GBC300, GBC400 and GBC500; as the pH increased to the weakly acidic/neutral (pH 5-

7), the adsorption capacities increase significantly, and the performance advantage of Se-GBC400 becomes most pronounced; in the near-neutral to weakly alkaline range (pH 7-9), Se-GBC400 reaches its maximum adsorption capacity (19.97 mg/g at pH 9), with a removal efficiency of 99.82%; at pH ≥ 10 , the adsorption capacities of all four GBCs converge to nearly the same value. For Se-GBC400 specifically, the Cd^{2+} adsorption capacity increased by 54.13% (from 9.16 mg/g at pH 2 to 19.97 mg/g at pH 9) with rising pH, a trend consistent with other biochar systems (Xu *et al.*, 2024). The pH-dependent adsorption behavior can be explained by two key factors: (1) Under highly acidic conditions, a high concentration of H^+ ions competes with Cd^{2+} for binding sites on the biochar surface, protonating oxygen-containing functional groups (e.g., $-\text{COOH} \rightarrow -\text{COOH}^{2+}$) and suppressing complexation and ion exchange; (2) As the pH rises, the concentration of competing H^+ decreases, the biochar surface deprotonates to form negative charges (e.g., $-\text{COO}^-$), which enhances electrostatic attraction towards cationic Cd^{2+} , and the decreased concentration of other competing cations (e.g., K^+ , Ca^{2+}) in solution further favors Cd^{2+} uptake. The superior adsorption performance of Se-GBC400 under acidic conditions is attributed to its higher content of oxygen-containing and Se-containing functional groups, which have stronger complexation ability with Cd^{2+} and are less susceptible to protonation compared to unmodified GBCs.

3.3.4 Effects of Adsorbent Dosage on Cd^{2+} Adsorption

The effect of biochar dosage on Cd^{2+} adsorption is shown in Fig. 5b. As the dosage increased from 0.05 g to 0.4 g, the Cd^{2+} removal rates for GBC300, GBC400, GBC500, and Se-GBC400 rose from 52.08%, 55.32%, 51.69%, and 51.32% to 99.36%, 99.52%, 99.23%, and 99.52%, respectively; When the dosage was further increased from 0.4 g to 1.6 g, the removal efficiency stabilized near 100%, while the adsorption capacity per unit mass of biochar exhibited a continuous decline. This inverse relationship

between dosage and unit adsorption capacity is typical phenomenon in adsorption systems, attributed to two main factors (Zhang et al., 2023): (1) with a fixed initial Cd^{2+} concentration, the total number of adsorbate ions is limited; as more adsorbent is added, the available adsorption sites surpass the number of Cd^{2+} ions, leading to site underutilization; (2) At higher dosages, biochar particle aggregation and overlapping of active sites reduce the effective surface area available per unit mass, further decreasing the specific adsorption capacity. Notably, at a dosage of 0.1 g (the optimal dosage for practical application), the adsorption capacity of Se-GBC400 for Cd^{2+} is significantly higher than that of the unmodified biochars, which confirms the practical application value of Se-GBC400 for Cd^{2+} remediation-its high unit adsorption capacity allows for lower dosage to achieve high removal efficiency, reducing the application cost of the adsorbent.

3.4 Adsorption Mechanisms of Cd^{2+} by Se-GBC400

The preceding results demonstrate that modification with Na_2SeO_3 increased both the average pore size and the surface concentration of OFGs in GBC400. Kinetics and isotherm analyses indicated that the adsorption of Cd^{2+} onto Se-GBC400 was predominantly a monolayer chemisorption process. To further elucidate the underlying mechanisms, the products of GBC400 and Se-GBC400 after Cd^{2+} adsorption were subsequently characterized by XRD, FTIR, and XPS.

3.4.1 XRD Analysis of Cd^{2+} by GBC400 and Se-GBC400

The XRD patterns of GBC400-Cd and Se-GBC400-Cd were presented in Fig. 6a. New diffraction peaks emerge at $2\theta = 30.27^\circ$, 36.33° , and 49.91° in both samples, corresponding to the (104), (110), and (116) planes of crystalline CdCO_3 . Notably, a sharp peak at 23.63° confirms the formation of CdCO_3 on biochar surfaces, indicating that Cd^{2+} adsorption occurred, in part, via a precipitation mechanism. It was proposed that CaCO_3 , identified as a primary crystalline phase in the pristine biochars, reacted with

Cd²⁺ in solution to form CdCO₃, a mechanism supported by studies on other carbonate-rich modified biochars (Zhang *et al.*, 2023). Intriguingly, the intensity of the CdCO₃ diffraction peaks is lower for Se-GBC400-Cd than for GBC400-Cd. Given that Se-GBC400 exhibited a significantly higher overall Cd²⁺ adsorption capacity (Fig. S1), this result strongly suggested that precipitation as CdCO₃ is not the dominant mechanism for the enhanced adsorption performance of the modified biochar. Instead, the superior adsorption capacity of Se-GBC400 is mainly due to the synergistic effect of surface complexation (via OFGs and Se-O groups) and ion exchange, which are enhanced by Na₂SeO₃ modification, and the optimized macroporous structure that reduces Cd²⁺ diffusion resistance.

3.4.2 FTIR Analysis of Cd²⁺ by GBC400 and Se-GBC400

The FTIR spectra of GBC400 and Se-GBC400 before and after Cd²⁺ adsorption were shown in Fig. 6b. Distinct changes in the spectra of Se-GBC400-Cd compared to GBC400-Cd highlight the influence of Na₂SeO₃ modification on the adsorption process. In the spectra of the pristine adsorbents, characteristic peaks were observed at: ~3435 cm⁻¹ (-OH stretching of alcohols/phenols), ~1619 cm⁻¹ (C=O/C=C stretching of carbonyls/aromatics), ~1415 cm⁻¹ (aromatic C=C skeletal vibrations), ~1146 cm⁻¹ (C-O stretching from lignocellulosic components), and ~873 cm⁻¹ (aromatic C-H bending).

Following Cd²⁺ adsorption, significant shifts and intensity changes occurred in these peaks. While changes in the -OH band were minimal, the C=O peak at ~1619 cm⁻¹ exhibited marked weakening and broadening. This suggested that Cd²⁺ preferentially interacts with carboxyl (-COOH) groups, forming stable Cd bound to oxygen (Cd-O) complexes and altering the carbonyl bond environment (Gao *et al.*, 2023). Concurrently, significant shifts were observed for the C-O and aromatic C-H bands. These shifts can be attributed to the coordination of Cd²⁺ with oxygen lone pairs from OFGs to form Cd-O-C bonds, and to π -Cd interactions between Cd²⁺ cations and the π -electron cloud of aromatic C=C systems. The π -

Cd interaction perturbs the vibration of adjacent aromatic C-H bonds, accounting for the observed enhancement in the $\sim 873\text{ cm}^{-1}$ band.

A critical finding was the shift of the Se-O vibration from $\sim 579\text{ cm}^{-1}$ in Se-GBC400 to $\sim 616\text{ cm}^{-1}$ in Se-GBC400-Cd, accompanied by an increase in intensity. This provided a direct spectroscopic evidence that selenium-oxygen functional groups participate in binding Cd^{2+} . The FTIR analysis revealed that Cd^{2+} adsorption onto Se-GBC400 involves a synergistic combination of mechanisms: surface complexation with carboxyl and other OFGs (C=O, C-O, Se-O), π -Cd interactions with aromatic structures, and likely cation- π interactions.

3.4.3 XPS Analysis of Cd^{2+} by GBC400 and Se-GBC400

The XPS survey spectra of the Cd-loaded biochars were shown in Fig. 6c. The appearance of a distinct Cd3d peak at a binding energy of approximately 406 eV confirms the successful adsorption of Cd^{2+} onto both GBC400 and Se-GBC400. The higher Cd3d peak intensity for Se-GBC400-Cd correlated with its superior adsorption capacity measured in batch experiments (Fig. 4).

In the survey spectrum of Se-GBC400-Cd, a decrease in the K2p signal intensity was observed. This was consistent with an ion exchange mechanism, where Cd^{2+} ions from solution displace K^{+} ions from the biochar surface, a pathway documented in other biochar systems. That Cd^{2+} adsorption occurred via ion exchange with residual cations (e.g., K^{+} , Mg^{+} , Ca^{2+}) present in pinecone and pine needle-based biochar (PRBs). This pathway made up 23.6% of the total Cd^{2+} adsorption capacity reported in their work (Park *et al.*, 2019). The observed decrease in the K2p peak within the XPS survey spectrum of Se-GBC400-Cd is likely attributed to an ion exchange reaction between Cd^{2+} and K^{+} , resulting in a reduction of the K element within the Se-GBC400.

High-resolution scans of the Cd3d region (Fig. 6d) provide further mechanistic insight. The spectrum was deconvoluted into two primary components. The peaks at approximately 406 eV and 413 eV were assigned to Cd3d_{5/2} and Cd3d_{3/2}, respectively, in an electronic environment indicative of π -Cd interactions (e.g., with aromatic structures in the biochar). The peaks at slightly higher binding energies (~407 eV and ~412 eV) correspond to Cd-O, suggesting complexation with surface functional groups.

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Quantitative analysis of these components revealed that the proportion of Cd associated with π -interactions increased from 43.96% in GBC400-Cd to 60.32% in Se-GBC400-Cd. This significant increase demonstrated that selenite modification enhanced the biochar's capacity for π -Cd interactions, which is a key factor in its improved performance. This trend aligned with findings for other modified biochars where π -interactions dominate Cd²⁺ uptake. In the findings reported that biochar produced through microwave pyrolysis of the poplar sawdust at temperatures from 400 to 800°C exhibited a similar peak in the Cd3d fine spectra after adsorbing Cd²⁺, and the π -Cd contribution reached 68.86% (Cheng *et al.*, 2021).

The high-resolution XPS spectra of the C1s, O1s, and N1s regions provide detailed evidence for the involvement of specific functional groups in Cd²⁺ adsorption (Fig. 7). After adsorption, significant changes were observed in the binding energies and relative peak areas of components such as C-O, C=O, and N-O in both GBC400-Cd and Se-GBC400-Cd. These changes indicated that OFGs, including

carboxyl and hydroxyl groups, donate lone electron pairs to form coordination complexes with Cd^{2+} . In the C1s spectra, a notable decrease in the K2p signal suggested that K^+ ions were displaced from the biochar surface via ion exchange with Cd^{2+} , corroborating the trend observed in the survey spectra. This mechanism was supported by similar findings in other biochar systems. (Huang et al., 2025). also observed a reduction in the peak area of K2p following the adsorption of Cd^{2+} by *A. cochinchinensis* straw biochar. (Tang et al., 2025) reported that after the adsorption of 2,4-D onto phosphoric acid and ammonia-modified biochar, the proportion of pyridinic nitrogen and pyrrolic nitrogen decreased. In the present study, after the adsorption of Cd^{2+} by Se-GBC400 and GBC400, the proportions of C=N and C-N in the N1s spectrum of Se-GBC400 decreased much greater than that of GBC400. This observation suggested that the introduction of Na_2SeO_3 enhanced the lone electron pair of C=N in GBC400. As a result, the interaction between Cd^{2+} and the π -electrons of aromatic rings was strengthened through π - π interactions. The greater reduction in C=N and C-N contents in Se-GBC400 further indicated that Se modification promoted the participation of nitrogen-containing functional groups in Cd^{2+} adsorption. Compared to GBC400-Cd, Se-GBC400-Cd exhibited a greater increase in the peak area corresponding to OFGs. This suggested that more OFGs in Se-GBC400 were involved in the adsorption process.

4 Conclusions

This study successfully developed a selenite-modified biochar (Se-GBC400) from grapevine pruning waste, optimized at a pyrolysis temperature of 400°C with a Se: GBC mass ratio of 1:1500, for the efficient remediation of Cd^{2+} contamination. Characterization of the pristine and modified materials revealed a key trade-off: while Na_2SeO_3 modification slightly reduced the specific surface area, which significantly increased the average pore diameter to 54.47 nm, thereby enhancing pore accessibility for Cd^{2+} ions. More critically, the modification enriched the biochar surface with Se-O functionalities and

amplified the intensity of existing surface functional groups such as -OH, -COOH, and CO_3^{2-} . This engineered surface chemistry facilitated superior Cd^{2+} adsorption through a synergistic combination of mechanisms: ion exchange (evidenced by K^+ displacement), surface complexation with oxygen functional groups, and π -Cd interactions with aromatic structures. Kinetic and isotherm analyses confirmed that the adsorption follows a monolayer chemisorption model on a heterogeneous surface.

This work demonstrated a dual-value strategy for sustainable agriculture. It transformed orchard waste into a high-value adsorbent for heavy metal remediation while simultaneously introducing the essential trace element selenium into the water environment. The approach of loading trace amounts of selenium onto biochar presents a promising pathway for the integrated resource recovery of agricultural by-products and water quality amendment.

Author Statement

Ting Du: Writing-original draft, Formal analysis, Conceptualization; **Shuxian An:** Data curation, Methodology, Software; **Hanbing Tian:** Investigation, Formal analysis; **Qingjie Li:** Software, Visualization, Methodology; **Jing Yan:** Supervision; **Xiaoqin Wang:** Writing-review & editing; **G S K Zackariah:** Writing-review & editing; **Zhigang Dong :** Writing-review & editing; **Jianqiang Yang:** Writing-review & editing; **Zhaojun Li:** Writing-review & editing, Funding acquisition, Supervision.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare no known competing financial interests/personal relationships which may be considered as potential competing interests.

454 **References**

- 455 Beigmohammadi, F., Solgi, E., Besalatpour, A. A., & Soleimani, M. (2024). Immobilization of
456 potentially toxic elements by grape waste biochar in contaminated soils. *Geoderma Regional*, 39.
457 <https://doi.org/10.1016/j.geodrs.2024.e00900>

458 Chen, J., Wang, N., Zhang, Z., Zhang, L., Fei, Q., & Ma, Y. (2022). New insights into wine waste
 459 management: Zero waste discharge-driven full energy/resource recovery strategy. *Results in*
 460 *Engineering*, 15. <https://doi.org/10.1016/j.rineng.2022.100606>

461 Cheng, S., Liu, Y., Xing, B., Qin, X., Zhang, C., & Xia, H. (2021). Lead and cadmium clean removal
 462 from wastewater by sustainable biochar derived from poplar saw dust. *Journal of Cleaner*
 463 *Production*, 314. <https://doi.org/10.1016/j.jclepro.2021.128074>

464 Deng, Y., Li, M., Zhang, Z., Liu, Q., Jiang, K., Tian, J., Zhang, Y., & Ni, F. (2021). Comparative study
 465 on characteristics and mechanism of phosphate adsorption on Mg/Al modified biochar. *Journal of*
 466 *Environmental Chemical Engineering*, 9(2). <https://doi.org/10.1016/j.jece.2021.105079>

467 Dorosh, O., Peixoto, A. F., Delerue-Matos, C., Castro, P. M. L., & Moreira, M. M. (2025). Optimizing
 468 Vineyard Pruning Biochars for Nutrient Adsorption: Toward Sustainable Fertilizer Applications.
 469 *Environments*, 12(12). <https://doi.org/10.3390/environments12120491>

470 Fan, S., Zhao, M., Luo, J., Li, W., Fan, X., Zhou, N., Xu, H., & Shi, Y. (2025). Facile preparation of N/P
 471 co-doped mesoporous biochar for efficient removal of methylene blue from aqueous solutions: A
 472 2D-FTIR-COS, adsorption mechanism analysis, and fixed-bed column study. *Journal of Water*
 473 *Process Engineering*, 72. <https://doi.org/10.1016/j.jwpe.2025.107479>

474 Feng, Q., Chen, M., Wu, P., Zhang, X., Wang, S., Yu, Z., & Wang, B. (2022). Simultaneous reclaiming
 475 phosphate and ammonium from aqueous solutions by calcium alginate-biochar composite: Sorption
 476 performance and governing mechanisms. *Chemical Engineering Journal*, 429.
 477 <https://doi.org/10.1016/j.cej.2021.132166>

478 Gao, Z., Shan, D., He, J., Huang, T., Mao, Y., Tan, H., Shi, H., Li, T., & Xie, T. (2023). Effects and
 479 mechanism on cadmium adsorption removal by CaCl₂-modified biochar from selenium-rich straw.

480 *Bioresour Technol*, 370, 128563. <https://doi.org/10.1016/j.biortech.2022.128563>

481 Hamzenejad Taghlidabad, R., & Sepehr, E. (2018). Heavy metals immobilization in contaminated soil
 482 by grape-pruning-residue biochar. *Archives of Agronomy and Soil Science*, 64(8), 1041–1052.
 483 <https://doi.org/10.1080/03650340.2017.1407872>

484 Huang, H., Jian, J., Tao, S., Gao, Z., Yan, C., Shangguan, Y., Xu, H., & Liu, H. (2025). Dual benefits of
 485 resource recycling and pollution mitigation: Enhanced cadmium adsorption using modified biochar
 486 from traditional Chinese medicine straw. *Journal of Environmental Chemical Engineering*, 13(2).
 487 <https://doi.org/10.1016/j.jece.2025.115592>

488 Huang, H., Li, M., Rizwan, M., Dai, Z., Yuan, Y., Hossain, M. M., Cao, M., Xiong, S., & Tu, S. (2021).
 489 Synergistic effect of silicon and selenium on the alleviation of cadmium toxicity in rice plants.
 490 *Journal of Hazardous Materials*, 401. <https://doi.org/10.1016/j.jhazmat.2020.123393>

491 Huang, Y., He, Y., Zhang, H., Wang, H., Li, W., Li, Y., Xu, J., Wang, B., & Hu, G. (2022). Selective
 492 adsorption behavior and mechanism of phosphate in water by different lanthanum modified biochar.
 493 *Journal of Environmental Chemical Engineering*, 10(3). <https://doi.org/10.1016/j.jece.2022.107476>

494 Ibn Ferjani, A., Jeguirim, M., Jellali, S., Limousy, L., Courson, C., Akrou, H., Thevenin, N., Ruidavets,
 495 L., Muller, A., & Bennici, S. (2019). The use of exhausted grape marc to produce biofuels and
 496 biofertilizers: Effect of pyrolysis temperatures on biochars properties. *Renewable and Sustainable*
 497 *Energy Reviews*, 107, 425–433. <https://doi.org/10.1016/j.rser.2019.03.034>

498 Lan, W., Zhao, X., Wang, Y., Jin, X., Ji, J., Cheng, Z., Yang, G., Li, H., & Chen, G. (2024). Research
 499 progress of biochar modification technology and its application in environmental remediation.
 500 *Biomass and Bioenergy*, 184. <https://doi.org/10.1016/j.biombioe.2024.107178>

501 Li, H.-y., Yao, D.-h., Feng, Q.-j., Zeng, H.-b., Liang, J.-m., Zhou, Z., Tian, Y., Zhou, N., & Lu, X.-y.

(2018). Adsorption of Cd(II) and Pb(II) on biochars derived from grape vine shoots. *Desalination and Water Treatment*, 118, 195–204. <https://doi.org/10.5004/dwt.2018.22414>

Li, S., Luo, C., Yan, F., Yang, Y., Guo, B., Wang, L., Xu, S., Wu, F., & Ji, P. (2023). Remediation of Pb(II) and Cd(II) in polluted waters with calcium thioglycolate–modified straw biochar. *Environmental Pollution*, 338. <https://doi.org/10.1016/j.envpol.2023.122638>

Liu, J., Huang, Z., Chen, Z., Sun, J., Gao, Y., & Wu, E. (2020). Resource utilization of swine sludge to prepare modified biochar adsorbent for the efficient removal of Pb(II) from water. *Journal of Cleaner Production*, 257. <https://doi.org/10.1016/j.jclepro.2020.120322>

Ma, F., Zhao, H., Zheng, X., Zhao, B., Diao, J., & Jiang, Y. (2023). Enhanced adsorption of cadmium from aqueous solution by amino modification biochar and its adsorption mechanism insight. *Journal of Environmental Chemical Engineering*, 11(3). <https://doi.org/10.1016/j.jece.2023.109747>

Mei, Y., Xu, J., Zhang, Y., Li, B., Fan, S., & Xu, H. (2021). Effect of Fe-N modification on the properties of biochars and their adsorption behavior on tetracycline removal from aqueous solution. *Bioresour Technol*, 325, 124732. <https://doi.org/10.1016/j.biortech.2021.124732>

Park, J.-H., Wang, J. J., Kim, S.-H., Kang, S.-W., Jeong, C. Y., Jeon, J.-R., Park, K. H., Cho, J.-S., Delaune, R. D., & Seo, D.-C. (2019). Cadmium adsorption characteristics of biochars derived using various pine tree residues and pyrolysis temperatures. *Journal of Colloid and Interface Science*, 553, 298–307. <https://doi.org/10.1016/j.jcis.2019.06.032>

Prelac, M., Palcic, I., Cvitan, D., Andelini, D., Repajic, M., Curko, J., Kovacevic, T. K., Goreta Ban, S., Uzila, Z., Ban, D., & Major, N. (2023). Biochar from Grapevine Pruning Residues as an Efficient Adsorbent of Polyphenolic Compounds. *Materials (Basel)*, 16(13). <https://doi.org/10.3390/ma16134716>

524 Qi, C., Zhang, C., Yang, Z., Liu, N., Gao, Y., Wang, R., Huang, D., Tian, F., Li, W., Wei, C., & Wu, Z.
 525 (2025). Acid-modified biochar-based bacterial fertilizer and increase soil available phosphorus.
 526 *Journal of Soils and Sediments*, 25(1), 59–66. <https://doi.org/10.1007/s11368-024-03937-0>
 527 Sun, X., Wei, X., Zhang, J., Ge, Q., Liang, Y., Ju, Y., Zhang, A., Ma, T., & Fang, Y. (2020). Biomass
 528 estimation and physicochemical characterization of winter vine prunings in the Chinese and global
 529 grape and wine industries. *Waste Management*, 104, 119–129.
 530 <https://doi.org/10.1016/j.wasman.2020.01.018>
 531 Tang, L., Chen, S., Wang, N., & Jiang, X. (2025). Comparative study of adsorption and slow-release
 532 performance and mechanism of phosphoric acid and ammonia-modified biochars on 2,4-
 533 dichlorophenoxyacetic acid. *Separation and Purification Technology*, 358.
 534 <https://doi.org/10.1016/j.seppur.2024.130470>
 535 Thommes, M., Kaneko, K., Neimark, A. V., Olivier, J. P., Rodriguez-Reinoso, F., Rouquerol, J., & Sing,
 536 K. S. W. (2015). Physisorption of gases, with special reference to the evaluation of surface area and
 537 pore size distribution (IUPAC Technical Report). *Pure and Applied Chemistry*, 87(9-10), 1051–
 538 1069. <https://doi.org/10.1515/pac-2014-1117>
 539 Velez, M., Murillo, H. A., Debut, A., Ducos, P., Niebieskikwiat, D., Torres, F. J., & Ponce, S. (2025).
 540 Green synthesis of Co–Ag biochar catalysts from rice husk using hydrothermal carbonization
 541 concentrate for efficient NaBH₄ hydrolysis. *Journal of Environmental Chemical Engineering*, 13(6).
 542 <https://doi.org/10.1016/j.jece.2025.120410>
 543 Wang, T., Zhang, D., Fang, K., Zhu, W., Peng, Q., & Xie, Z. (2021). Enhanced nitrate removal by physical
 544 activation and Mg/Al layered double hydroxide modified biochar derived from wood waste:
 545 Adsorption characteristics and mechanisms. *Journal of Environmental Chemical Engineering*, 9(4).

546 <https://doi.org/10.1016/j.jece.2021.105184>

547 Wang, W., Jiang, H., Tan, Z., Yu, L., Chen, J., Xiao, Q., Rong, Q., & Zhou, C. (2025). Selenium-Modified

548 Biochar Synergistically Achieves the Safe Use of Selenium and the Inhibition of Heavy Metal

549 Cadmium. *Molecules*, 30(2). <https://doi.org/10.3390/molecules30020347>

550 Wong, M. C., Hendrikse, S. I. S., Sherrell, P. C., & Ellis, A. V. (2020). Grapevine waste in sustainable

551 hybrid particleboard production. *Waste Management*, 118, 501–509.

552 <https://doi.org/10.1016/j.wasman.2020.09.007>

553 Wu, S., Wang, Q., Cui, D., Wu, D., Bai, J., Qin, H., Xu, F., & Wang, Z. (2023). Insights into the chemical

554 structure evolution and carbonisation mechanism of biomass during hydrothermal treatment.

555 *Journal of the Energy Institute*, 108. <https://doi.org/10.1016/j.joei.2023.101257>

556 Xu, H., Zhou, Q., Yan, T., Jia, X., Lu, D., Ren, Y., & He, J. (2024). Enhanced removal efficiency of Cd²⁺

557 and Pb²⁺ from aqueous solution by H₃PO₄-modified tea branch biochar: Characterization,

558 adsorption performance and mechanism. *Journal of Environmental Chemical Engineering*, 12(2).

559 <https://doi.org/10.1016/j.jece.2024.112183>

560 Yan, J., Guo, X., Li, Q., Yuan, X., Zhang, Z., Tremblay, L. A., & Li, Z. (2024). Biochar derivation at low

561 temperature: A novel strategy for harmful resource usage of antibiotic mycelial dreg. *Environ Res*,

562 250, 118376. <https://doi.org/10.1016/j.envres.2024.118376>

563 Yang, C., Liu, J., & Lu, S. (2021). Pyrolysis temperature affects pore characteristics of rice straw and

564 canola stalk biochars and biochar-amended soils. *Geoderma*, 397.

565 <https://doi.org/10.1016/j.geoderma.2021.115097>

566 Yang, T., Xu, Y., Huang, Q., Sun, Y., Liang, X., & Wang, L. (2022). Removal mechanisms of Cd from

567 water and soil using Fe-Mn oxides modified biochar. *Environ Res*, 212(Pt C), 113406.

568 <https://doi.org/10.1016/j.envres.2022.113406>

569 Yang, X., Kang, K., Qiu, L., Zhao, L., & Sun, R. (2020). Effects of carbonization conditions on the yield
570 and fixed carbon content of biochar from pruned apple tree branches. *Renewable Energy*, 146,
571 1691–1699. <https://doi.org/10.1016/j.renene.2019.07.148>

572 Zhang, K., Chen, Y., & Fang, Z. (2023). Highly Efficient Removal of Cadmium by Sulfur-Modified
573 Biochar: Process and Mechanism. *Water, Air, & Soil Pollution*, 234(1).
574 <https://doi.org/10.1007/s11270-022-06005-w>

575 Zhang, P., Zhang, X., Yuan, X., Xie, R., & Han, L. (2021). Characteristics, adsorption behaviors, Cu(II)
576 adsorption mechanisms by cow manure biochar derived at various pyrolysis temperatures.
577 *Bioresour Technol*, 331, 125013. <https://doi.org/10.1016/j.biortech.2021.125013>

578 Zhang, T., Li, W., Luo, J., Zhao, M., Wang, Y., & Fan, S. (2025). Magnetic mesoporous corncob biochar
579 for tetracycline adsorption: 2D-FTIR-COS analysis and quantitative mechanistic insight. *Colloids
580 and Surfaces A: Physicochemical and Engineering Aspects*, 723.
581 <https://doi.org/10.1016/j.colsurfa.2025.137378>

582 Zhang, Y., Zhang, L., Han, C., Ren, Y., Ji, Y., Ge, Y., Li, Z., & He, J. (2023). Preparation, characteristics
583 and mechanisms of Cd(II) adsorption from aqueous solution by mango kernel-derived biochar.
584 *Biomass Conversion and Biorefinery*, 13(1), 393–407. [https://doi.org/10.1007/s13399-022-03050-](https://doi.org/10.1007/s13399-022-03050-7)
585 [7](https://doi.org/10.1007/s13399-022-03050-7)

586 Zhang, Z., Gao, S., & Shan, C. (2020). Effects of sodium selenite on the antioxidant capacity and the
587 fruit yield and quality of strawberry under cadmium stress. *Scientia Horticulturae*, 260.
588 <https://doi.org/10.1016/j.scienta.2019.108876>

589 Zhou, Q., Huang, Y., Liu, L., Li, Z., Xiao, Y., Li, Z., Tian, T., & Pan, H. (2025). Enhanced cadmium

adsorption by silicate-modified biochar derived from sawdust: Mechanisms and performance
analysis. *Surfaces and Interfaces*, 65. <https://doi.org/10.1016/j.surfin.2025.106430>
Zhu, Y., Yang, T. X., Li, H., Zhao, Q. S., & Zhao, B. (2024). Synergism of jet milling and deep eutectic
solvent pretreatment on grapevine lignin fractionation and enhancing enzymatic hydrolysis. *Int J*
Biol Macromol, 269(Pt 2), 132144. <https://doi.org/10.1016/j.ijbiomac.2024.132144>

Figure captions

Fig.1 SEM images of GBCs (a. GBC300; b. GBC400; c. GBC500; d. Se-GBC400).

Fig.2 XRD Patterns (a), FTIR Spectra (b), and XPS Survey Spectra (c) of GBCs before and after
modification.

605 **Fig.3** High-resolution spectra of C1s (a,b), O1s (c,d) and N1s (e,f) of GBCs before and after
606 modification.

607 **Fig.4** Fitting results of adsorption kinetics (a), intra-particle diffusion (b), and adsorption isotherms (c)
608 for GBC before and after modification.

609 **Fig.5** Adsorption capacity and removal rate of Cd^{2+} by GBCs under different parameters before and
610 after modification (a. Different initial pH values of the solution; b. Different dosages of GBCs).

611 **Fig.6** XRD spectrum (a), FTIR spectrum (b), XPS spectrum (c) and Cd3d spectra (d) before and after
612 Cd^{2+} adsorption of GBC400 and Se-GBC400.

613 **Fig.7** Se3d spectra (a), C1s spectra (b), O1s spectra (c), and N1s spectra (d) of GBC400 and Se-
614 GBC400 after adsorption.

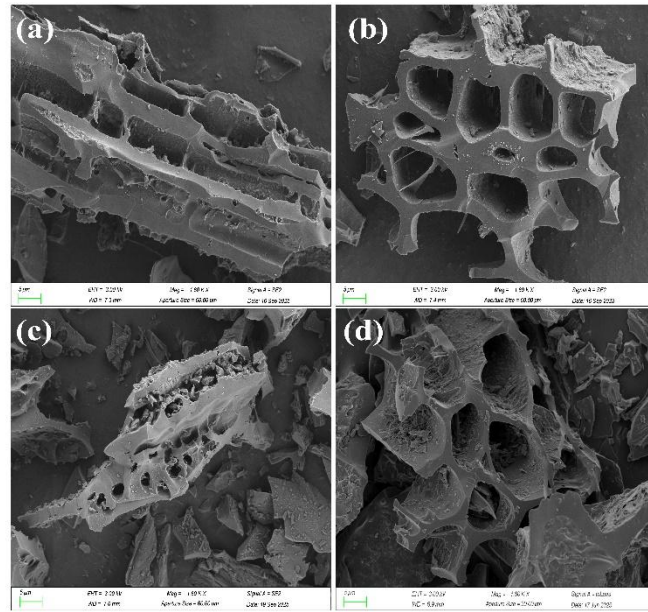


Fig.1

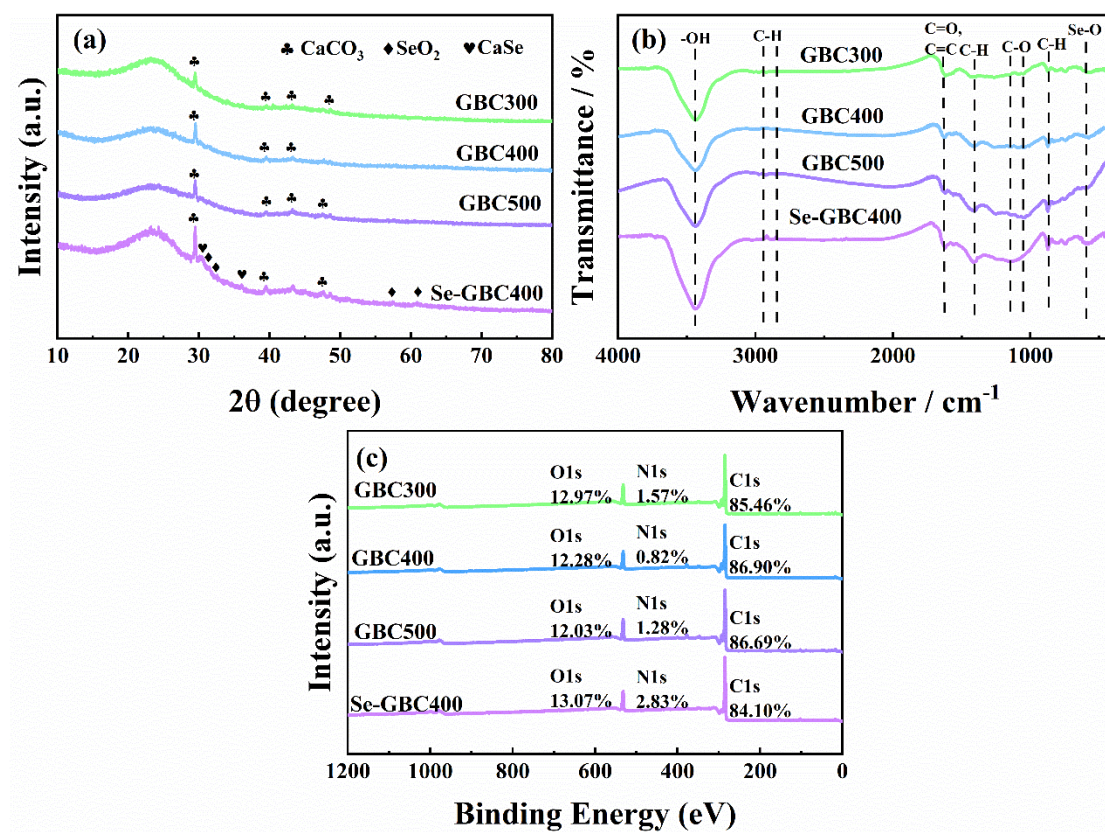


Fig.2

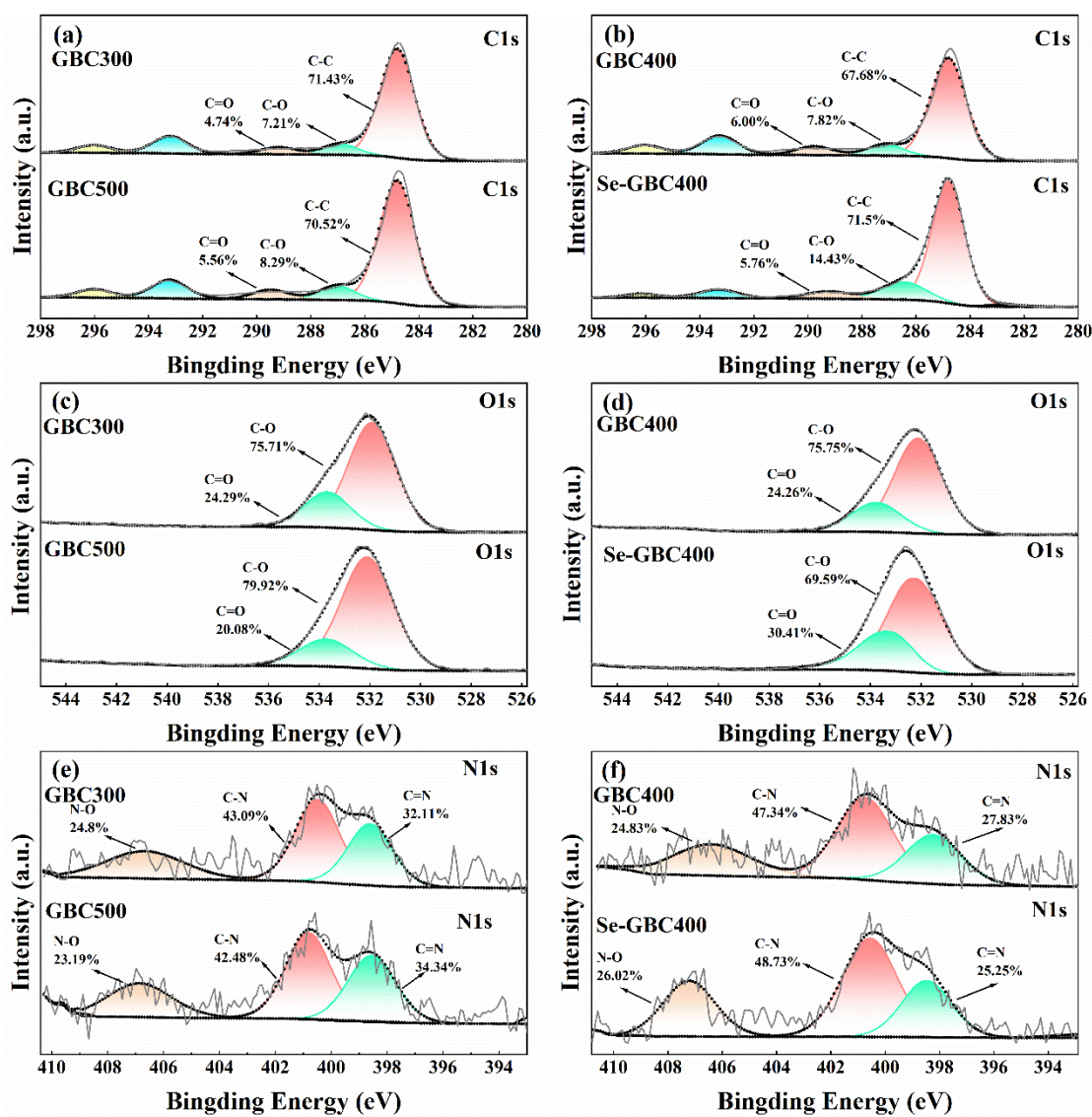


Fig.3

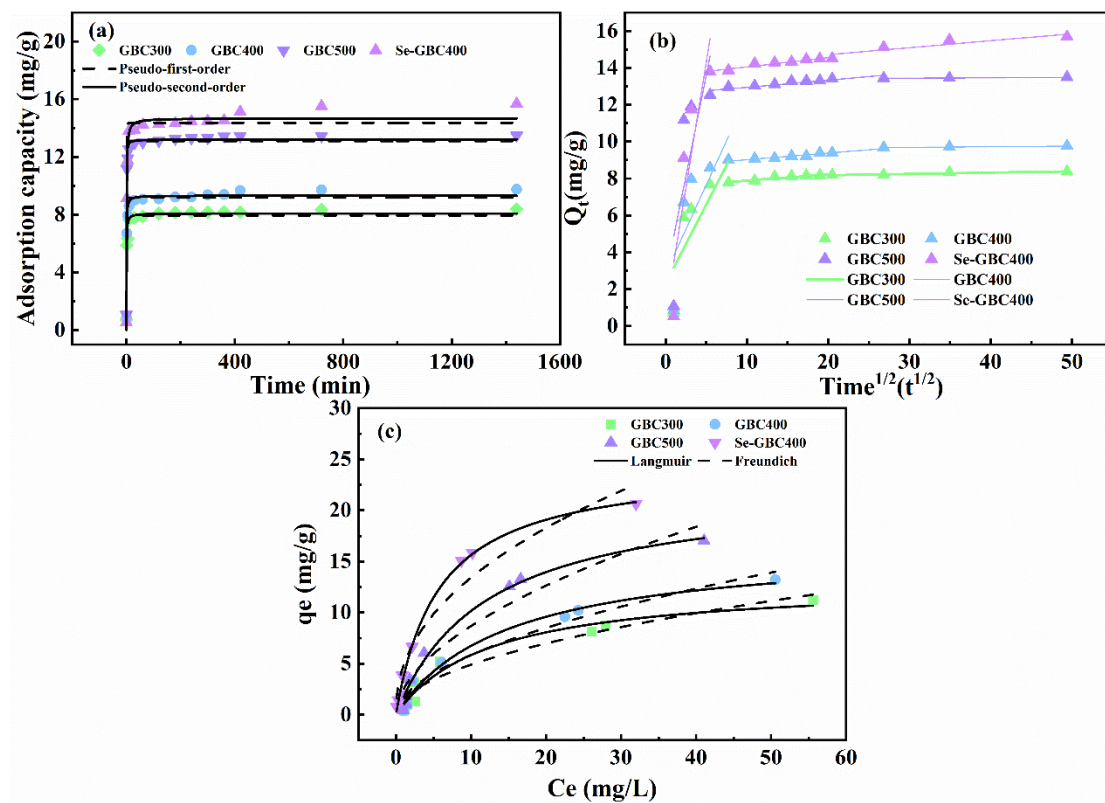


Fig.4

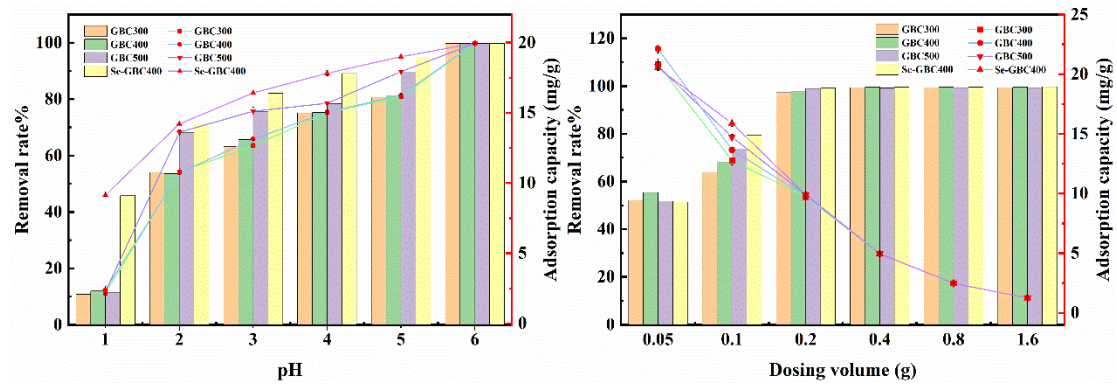


Fig.5

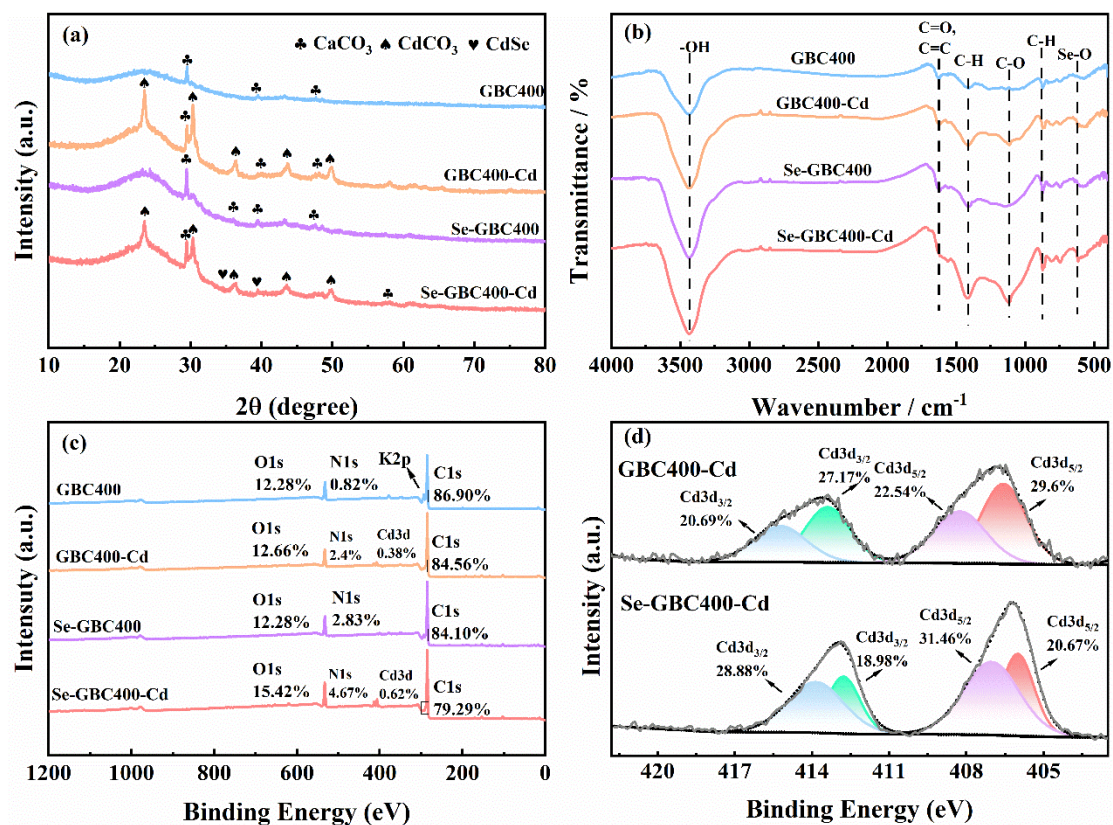


Fig.6

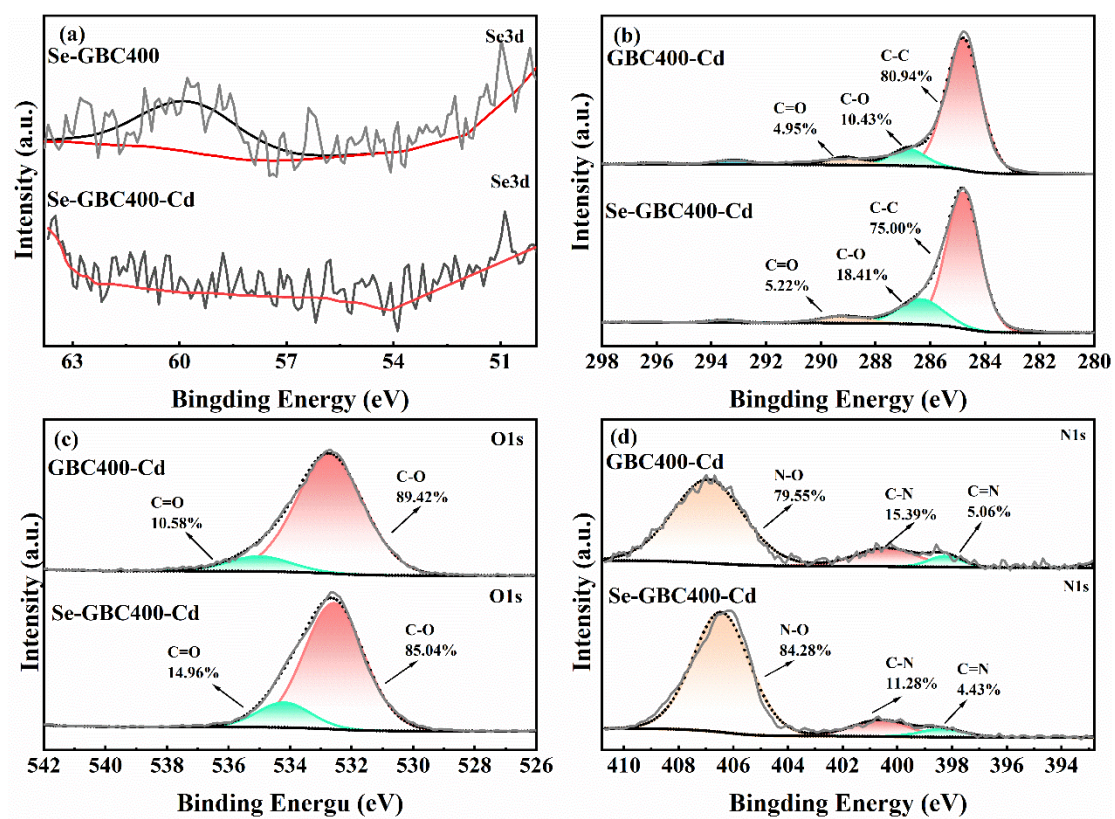


Fig.7

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