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Synthesis of eco-friendly bio-based coconut shell magnetic biochar for efficient bisphenol S sequestration in aqueous environment: green technology breakthrough

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ABSTRACT

Water pollution has emerged as a critical global challenge, particularly the contamination of water bodies with persistent organic pollutants such as Bisphenol S (BPS), a known endocrine disruptor. This study presents the synthesis and application of eco-friendly bio-based coconut shell magnetic biochar (CSMB) for efficient sequestration of BPS from aqueous environments. Utilizing pyrolysis and co-precipitation techniques, the magnetic biochar was characterized through various methods including surface chemistry (pHpzc), electron dispersive X-ray analysis (EDX), Brunauer-Emmett-Teller (BET) N₂ adsorption-desorption, scanning electron microscopy (SEM), vibrating sample magnetometer (VSM), and Fourier transform infrared spectroscopy (FTIR). SEM revealed a porous structure with a high surface area, while FTIR confirmed the presence of functional groups essential for adsorption. X-ray diffraction (XRD) and VSM successfully incorporated magnetic nanoparticles, enhancing the separation process post-adsorption. The CSMB demonstrated a significant surface area of 373 m² g⁻¹, outperforming regular coconut shell biochar (CSB), with a BPS adsorption capacity of 43.5 mg/g compared to 26.7 mg/g for CSB. Batch adsorption tests assessed the impact of operational factors such as initial BPS concentration (8–150 ppm), contact time (30–150 min), temperature (298.15, 318.15, and 338.15 K), pH (3–11), and CSMB dosage (0.1–0.9 g). The results indicated optimal adsorption at pH 6 with a maximum capacity of 52.3 mg/g. Kinetic studies revealed that the pseudo-second-order model best described the adsorption process, while the Langmuir isotherm model provided an excellent fit for the adsorption data. The reusability of CSMB was validated over five cycles, with adsorption capacity decreasing slightly from 43.5 mg/g to approximately 41 mg/g, making it a sustainable and effective adsorbent for water treatment.

KEYWORDS

Adsorbent; adsorption; bisphenol S; coconut shell; magnetic biochar; regeneration

Introduction

Water pollution has become an emerging global threat to the safety and quality of drinking water. The availability of freshwater has become a major global environmental issue, presenting a critical challenge to the provision of affordable as well as safe, pristine drinking water across the world owing to rapid industrialization and urbanization with an emerging issue that is gradually threatening the environment (Al Sharabati et al. 2021). The release

of partially treated or untreated wastewater is considered among the leading causes of water pollution (Nasrollahzadeh et al. 2021; Saha et al. 2022). This indiscriminate release of untreated or partially treated wastewater contaminates pristine water bodies with emerging inorganic and organic pollutants, especially endocrine-disrupting compounds (EDCs) *via* wastewater discharge from plastics, thereby making plastic pollution a significant environmental hazard (Zhao and Sillanpää 2020). Since 2007, there have been several reports of Bisphenol

pollution from plastics (Vandenberg et al. 2007), and this anomaly has received growing interest from the scientific community as well as regulatory authorities owing to their prevalent incidences, distribution, acute toxicity, and adverse impacts (Lee et al. 2019).

Bisphenol S (BPS, 4,40-sulfonyl diphenol) was developed as a safe BPA alternative since authorities strictly controlled the utilization of BPA (Fang et al. 2020). Products made with BPS-based material possess superior thermal and mechanical stability, which has led to the manufacturing of approximately 1000–10,000 tonnes of this commodity in several European nations. (Morsi et al. 2019) as the principal replacement for BPA (Choi and Lee 2017). BPS is extensively utilized in industries for various purposes including lacquers, liners, adhesives, drink packages, plastics, food cans, and agricultural production (Cheng et al. 2021). Studies have indicated that the primary pathway for BPS can accrue within human beings and animal organisms *via* the food chain and wastewater treatment plant effluents, leading to the manifestation of various disorders within these organisms (Katibi et al. 2023). Pollution emanating from leachate from garbage disposal sites and chemical plants has been identified as the primary source of contamination by synthetic EDCs in aquatic ecosystems (Katibi et al. 2021), and are afterward released into sewage systems and water bodies. Recently, studies have detected the presence of bisphenol end product in municipal wastewater (Rezania et al. 2021). Among Bisphenols, BPS exhibits higher solubility in water (1100.0 ppm) compared to BPA (146.0 ppm) by a factor of 12, indicating that BPS is primarily found in aqueous environments (U.S. Environmental Protection Agency 2012). Several studies have reported the detrimental health consequences associated with exposure to EDCs, including a decline in sperm count, diminished fertility, and elevated rates of breast, ovarian, and testicular cancers (Bai and Acharya 2019; Ismail et al. 2019; Katibi et al. 2021). Also, Bisphenols induce corrosion in the skin, eyes, and lungs, leading to edema, seizures, dysrhythmia, and potential coma (Quan et al. 2019). Given the severe adverse effects of bisphenol derivatives on public health and the environment,

removing these persistent contaminants to safeguard public health becomes indispensable.

Numerous adsorbents have been developed to eliminate Bisphenols from water, including organoclays (Park et al. 2014), metal-organic frameworks (Rezania et al. 2021), β -Cyclodextrin-modified graphene oxide membranes (Chen et al. 2020), hematite nanoparticles (Katibi et al. 2022) and biochar carbonaceous-based materials (Jun et al. 2019).

Biochar (BC), a carbonaceous material with a porous structure derived from the pyrolysis of organic waste, has emerged as a promising adsorbent for confronting environmental pollution owing to its diverse sources, abundant surface functional groups, elevated porosity, and cost-effectiveness (Dai et al. 2023; Yi et al. 2019). Biochar is a three-dimensional (3D) carbon structure material characterized by its superfluous high surface area, porosity, and carbon-rich material that has attracted significant interest from various researchers.

Biochar has been widely utilized as an adsorbent to remove a wide range of contaminants from water. However, biochar is restricted due to its complexities associated with regeneration and reusability, hydrophobic surface properties, and stacking behavior, particularly undermining its efficacy in water treatment and scaled-up production (Wang et al. 2024; Xu et al. 2024). Also, the conventional method of separating BC powder from the environmental medium typically involves further steps such as centrifugation and filtration, which can undermine its practical applications and potentially lead to secondary pollution issues (Du et al. 2023; Niu et al. 2020; Oyekanmi et al. 2024). Consequently, recent studies have focused on integrating magnetic properties into adsorbents as an efficient recovery strategy to overcome these limitations.

Recently, there has been a development in magnetic technology, emerging as an alternative method for water purification (Soylak et al. 2021). This is especially evident in adsorption systems, where the focus is on addressing the challenges associated with the separation and recovery of powder adsorbents from solution (Chen et al. 2022; Soylik et al. 2021), consequently resulting in an extensive viable

application for removing pollutants from water. Magnetic separation presents numerous benefits in recovering adsorbents from water, including enhanced efficiency, facile synthesis procedure, and inexpensive. This method has been combined with several adsorbents to recycle and remove pollutants efficiently (Chen et al. 2022; Katibi et al. 2021; Yi et al. 2019).

Coconut shell-based magnetic biochar presents a superior alternative to other biochar types and traditional pollutant removal technologies owing to its renewable sourcing from abundant agricultural waste, large surface area, and high porosity augmented for efficient pollutant adsorption (Baby et al. 2019). By incorporating magnetic properties, this biochar facilitates direct separation from water systems, minimizing the need for complex and energy-intensive separation techniques and reducing operational costs and secondary pollution hazards (Huang et al. 2021). This innovation enhances the adsorption capacity for a broad spectrum of contaminants, including organic pollutants, and heavy metals, leveraging the biochar's innate surface functional groups and pore structure. Also, adsorption technology itself offers advantages such as high efficiency in contaminant removal, resourcefulness across different environmental matrices, negligible by-products, and cost-effectiveness, making it an essential approach in sustainable environmental remediation efforts (Deb et al. 2021).

This study presents an innovative approach to environmental remediation by developing eco-friendly magnetic biochar derived from coconut shells, aimed at highly efficient sequestration of BPS from aqueous environments. Exploiting the biodegradable and renewable properties of coconut shells, CSMB presents a sustainable alternative to traditional remediation materials and incorporates magnetic properties for enhanced separation and recovery post-treatment. This innovation is a significant advancement in green technology, addressing the urgent need for efficient and environmentally friendly solutions to water pollution. By achieving superior BPS removal efficiency compared to conventional methods, CSMB bio-based magnetic biochar promises practical water treatment and environmental protection applications, marking a breakthrough in sustainable technology

for mitigating industrial contaminants in aquatic ecosystems.

The application of magnetic biochar derived from coconut shell biobased materials in removing BPS using synthetic solutions has not been reported. However, insufficient studies report the removal of BPS using magnetic biochar synthesized from coconut shell biochar (CSB) from an aqueous solution. In this study, we assess adsorption performance for BPS, the effects of operational variables, including pH, contact time, and adsorbent dosage, on the BPS removal, kinetics, isotherms, and thermodynamic studies. The reusability of the adsorbent was also investigated, and the potential adsorption mechanisms were explored.

Materials and methods

Materials

Iron sulfate (FeSO_4), iron (III) chloride (FeCl_3), sodium hydroxide (NaOH), ethanol ($\text{C}_2\text{H}_5\text{OH}$), and hydrochloric acid (HCl) were sourced from Sigma-Aldrich Co. (MO, USA) and used. All chemicals used in this study were of analytical grade and were used without further purification. During the experiment, all aqueous solutions were prepared employing distilled water. The Sri Kembangan market, Selangor, Malaysia, provided the raw coconut shell (CS) used in the study. The raw material was gathered and dried in an oven at 105°C for 24 hrs before being stored at room temperature for the subsequent processes.

Preparation of magnetic biochar adsorbent

Coconut shells (CS) were broken down into smaller fragments measuring 20–25 mm using a mallet. After that, a crusher was employed to crush the material into larger macroscopic particles, and it was extensively washed and cleaned using acetone, both before and after utilization, to eliminate any potential contaminants and later dried. The crushed CS particles were milled into finer particles and sifted according to ASTM mesh standards. This sieving process was conducted using a KingTest Sieve with a diameter of 75 mm, operated on a KingTest Sieve Shaker (model VB 200/300) with a voltage rating of 220 V/ 50 Hz and a current rating of 5 A. Subsequently,

the CS undergoes a thorough cleaning process with distilled water to eliminate dust and sand particles, enhancing the quality of the sample. After the cleaning stage, the CS was dried under vacuum conditions at temperatures exceeding 135 °C for 12 h.

The CS was transformed into biochar using the precise slow pyrolysis procedure. Firstly, fresh CS was thoroughly rinsed with distilled water to obliterate undesirable foreign items and other impurities and dried at 120 °C overnight. The dried samples were then crushed into a smaller size. Subsequently, 25.0 g of ground precursor material derived from CS was subjected to pyrolysis within the temperature range of 200–600 °C for 3 h under a nitrogen (N₂) atmosphere flowing at a rate of 230 mL/min. Following this, the temperature of the heating element was gradually raised for one h at a rate of 5–10 °C/min and thereafter allowed to cool down (within 120–180 min) under N₂ flow until reaching ambient temperature, having been initially held at 500 °C for one h. The resulting product was then subjected to high-energy ball milling using a planetary ball mill (Nanjing University Instrument Co., China) equipped with stainless steel vials (80 mL) and 5.60 mm diameter balls weighing 120 g in each vial for a period of 3 h. The milled product was then sieved to achieve a particle size below 60 µm, followed by rinsing with distilled water and ethanol five times to eliminate any impurities present. Afterward, the washed biochar was dried in an oven at 120 °C overnight and transferred to dry using oxygen-free, airtight borosilicate glass vials of 80 mL capacity for subsequent applications. In the subsequent step, 16.5 g of the desiccated chitosan biochar was immersed in a solution comprising 0.25 mol. L⁻¹ of FeCl₃ and 100 mL of 0.125 mol. L⁻¹ of FeSO₄ solution, and continuously agitated using a magnetic stirrer. The resulting mixture underwent further heating at 60 °C with continuous stirring to facilitate the saturation of iron species (Fe²⁺/Fe³⁺) into the CS biochar, then left to cool to 40 °C. A 2.5-M NaOH solution was added drop by drop to the suspension under vigorous magnetic stirring until the pH of the mixture reached 10–11, transitioning from a brownish green to a black hue. This process led to the precipitation of Fe₃O₄ on the

surface of the biochar material under alkaline conditions. Upon completion of the reaction, the NaOH-saturated biochar solution was stirred adequately at 80 °C for 1 h to ensure a more homogeneous and dispersed mixture. The resulting solution was separated using an external magnet, rinsed with distilled water to adjust the pH to 7, and dried at 70 °C for 12 h. The final samples obtained were preserved in sealed containers and utilized in the subsequent adsorption experiments and biochar characterization. The outlined approach for synthesizing CSMB from CS as the precursor material is depicted in Figure 1.

Adsorbents measurements

The Fourier Transform Infrared (FTIR) spectroscopy was utilized to provide insights into the functional groups on the fabricated adsorbent. Employing the Bruker-Tensor 27 IR instrument following the standard KBr-pellet technique within the spectral region of 400–14000 cm⁻¹ at a resolution of 2 cm⁻¹ facilitated the identification of FTIR spectra about the adsorbent. In addition, the X-ray diffraction (XRD) methodology was employed to study the crystal structure and phase characteristics of the synthesized CSMB. This analysis was carried out using the X-ray diffraction (XRD) Philips Expert Diffractometer with Cu K α radiation (λ = 0.154 nm) across the 2 θ range of 10 to 70°, with a scan step size of 2 θ = 0.033 and a counting time of 5s per step.

Furthermore, the fabricated adsorbent's structural morphology was assessed by utilizing a NovaNano 230 Field-Emission Scanning Electron Microscope (FESEM). In contrast, the elemental compositions of the adsorbent were ascertained *via* energy dispersive spectroscopy (EDS) utilizing the Bruker/Quanta 200 system located in Westerville, OH, USA. The determination of the specific surface area of the adsorbent was conducted using the Braunauer-Emmett-Teller (BET) method with the Micromeritics II PLUS instrument in the USA through nitrogen adsorption-desorption isotherms, employing the NOVA2020e automatic surface area and porosity analyzer. Prior to the analysis, the adsorbent underwent degassing at 100 °C. The surface charge characteristics of the CSMB were investigated across varying pH values ranging

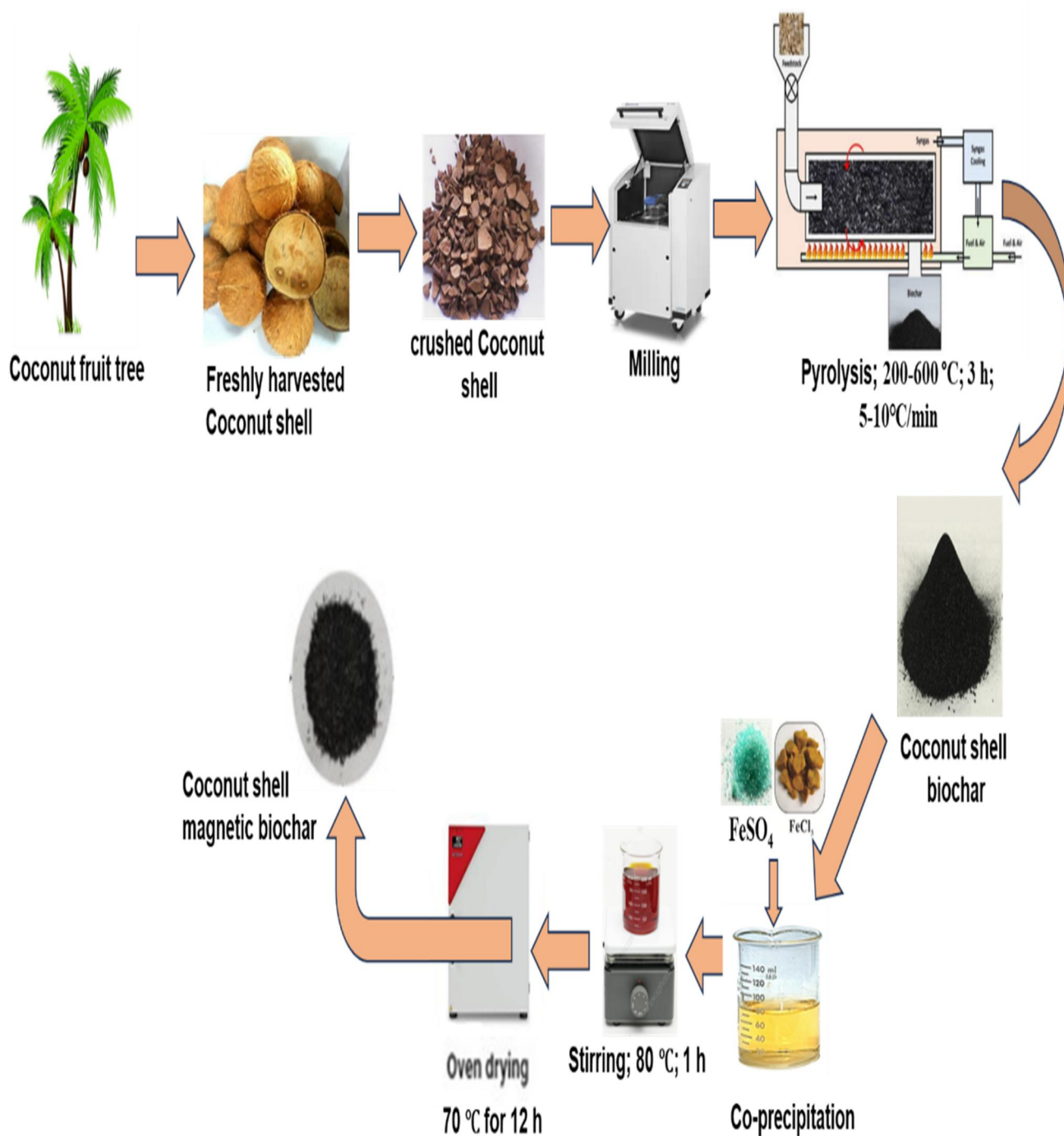


Figure 1. Synthesis procedure of CSMB.

from 2 to 11 (Oyekanmi et al. 2024). Experiments were conducted utilizing a 50 mL solution of 0.1 M KCl. The pH of the solution was adjusted using concentrations of 0.1 M NaOH and HCl. Each 100 ml portion of the pH-adjusted solution received 0.1 g of CSMB, which was then placed in a flask. The samples were shaken for 48 h at room temperature using a magnetic shaker. The pH_{pzc} value was determined by plotting the initial

solution pH against the supernatant pH and computing the intersection point (Hosain et al. 2020; Nnadozie and Ajibade 2020). The Zeta potential measurement was undertaken using a Zeta sizer (Malvern ZS, UK). The zeta sizer provided a titration of several pH values. The magnetic hysteresis properties of the CS magnetic biochar adsorbent were investigated using a vibrating sample magnetometer (VSM, LakeShore7404) under an applied

external magnetic field ranging from $-10,000$ Oe to $10,000$ Oe.

Batch adsorption study in an equilibrium condition

A fixed amount of CSMB adsorbents (50.0 mg) was measured using a digital balance, and 125.0 mL of BPS solution was prepared and distributed into a series of 250 mL Erlenmeyer flasks, which were sealed externally with aluminum foil to prevent potential photodegradation. These flasks were then placed on an orbital shaker (HY-8, Shanghai, China) and agitated mechanically at 180 rpm under room temperature for 24 h until equilibrium was reached. Upon completion of the agitation process, the solution was promptly poured off and filtered using a $0.4\mu\text{m}$ membrane. The absorbance of the resulting supernatants was then determined spectrophotometrically at 276 nm using a double-beam UV-visible spectrophotometer (Shimadzu UV-1800, Kyoto, Japan) equipped with a pair of 10 mm matched quartz cells. The concentrations were then determined based on the established BPS calibration curve.

In a factorial experiment, the influence of varying dosages of the adsorbent (CSMB) (0.1 , 0.3 , 0.5 , 0.7 , and 0.9 g; BPS: 20 ppm; pH: 7.0 , agitation speed: 300 rpm, temperature: 25°C), pH levels adjusted using 0.01 mol/L HCl and 0.01 mol/L NaOH solutions (ranging from 3.0 to 11.0 ; BPS = 20 ppm; temperature: 25°C ; dosage: 0.8 g; agitation speed: 300 rpm), contact time (30 , 60 , 90 , 120 , and 150 min; BPS: 20 ppm; pH: 7.0 , agitation speed: 300 rpm, dosage: 0.8 g temperature: 25°C), initial BPS concentrations (ranging from 8 to 150 ppm), pH: 7.0 , agitation speed: 300 rpm, dosage: 0.8 g; temperature: 25°C , and reaction temperatures (298.15 , 318.15 , and 338.15 K), BPS: 150 ppm, pH: 7.0 , dosage: 0.8 g; agitation speed: 300 rpm, on the adsorption of BPS by CSMB were investigated. To ensure result accuracy, each experiment was repeated thrice. The BPS adsorption percentage of the adsorbents was determined using Equation (1) (Saha, Shaji, et al. 2023):

$$\text{Adsorption (\%)} = \left(\frac{C_i - C_f}{C_i} \right) \times 100 \quad (1)$$

C_i and C_f represent the initial equilibrium and final concentrations of BPS (ppm), respectively. The BPS adsorption capacity was computed using the mass

balance Equation (2) (Sulaiman et al. 2021):

$$q_e = \frac{(C_i - C_e)V}{m} \quad (2)$$

In this context, C_e depicts the final and equilibrium concentration of BPS (ppm), q_e represents the adsorption capacity (mg/g), m is the weight of the adsorbent (g) and V is the volume of the BPS solution (L).

Isotherm model studies

Langmuir, Freundlich, and Temkin isotherms were employed to characterize BPS sorption onto CSMB. The Langmuir model postulates monolayer adsorption on a homogeneous surface without intermolecular interaction. Below is the non-linearized Langmuir isotherm Equation (Baby et al. 2019):

$$q_e = \frac{q_{\max} k_L C_e}{1 + k_L C_e} \quad (3)$$

Where, C_e =equilibrium concentration of BPS (ppm); $q_{\max}$ =maximum amount of BPS that can be adsorbed by biochar (mg/g); q_e =Amount of BPS adsorbed onto biochar (mg/g); k_L =Langmuir adsorption equilibrium constant (L/mg). The separation factor (R_L) was calculated using the Langmuir constant (K_L) obtained from the Langmuir isotherm model and the initial concentration (C_o) of BPS. To determine the favorability of the adsorption process, the dimensionless separation factor (R_L) was calculated using Equation (4) (Khattari and Singh 2009):

$$R_L = \frac{1}{1 + K_L C_o} \quad (4)$$

where K_L is the Langmuir constant (L/mg), and C_o is the initial concentration of BPS (ppm). The value of R_L indicates the nature of the adsorption process: if $R_L > 1$, the adsorption is unfavorable; if $R_L = 1$, the adsorption is linear; if $0 < R_L < 1$, the adsorption is favorable; and if $R_L = 0$, the adsorption is irreversible.

The Freundlich model represents an empirical equation used to describe chemisorption on heterogeneous surfaces. Below is the linearized Freundlich isotherm Equation (5) (Abba et al. 2021):

$$q_e = k_F C_e^{1/n} \quad (5)$$

Here, k_F represents the Freundlich adsorption equilibrium constant, and n indicates the adsorption intensity.

The Temkin isotherm Equation for a non-linear plot is described as (Sulaiman et al. 2021):

$$q_e = B \times \ln(A \times C_e) \quad (6)$$

Where q_e is the amount of adsorbate adsorbed per unit weight of adsorbent at equilibrium (mg/g), C_e is the equilibrium concentration of the adsorbate in the solution (ppm), A (L/g) is the Temkin isotherm constant related to the maximum binding energy, B (J/mol) is the Temkin isotherm constant related to the heat of adsorption. For the Temkin model, the constants A and B are computed by fitting the experimental data to this non-linear equation.

Adsorption kinetic study

To investigate the adsorption kinetics of BPS on the synthesized CSMB, batch adsorption experiments were conducted by varying the contact time from 30 to 150 min at an initial BPS concentration range of 8–150 ppm, maintaining a constant temperature (298.15, 318.15, and 338.15 K), and adjusting the pH to 6.0, which was found to be the optimal pH for adsorption. Different concentrations of BPS solutions were prepared by diluting a stock solution with distilled water. A known quantity (0.7 g) of CSMB was added to 125 mL of BPS solution in a series of 250 mL Erlenmeyer flasks. The flasks were sealed with aluminum foil to avoid photodegradation and agitated in an orbital shaker at 180 rpm at specified temperatures until equilibrium was achieved. Samples were withdrawn and filtered at predetermined intervals using a 0.45 μ m membrane filter. The residual concentration of BPS in the filtrate was determined using a UV-visible spectrophotometer at 276 nm. The experimental data were analyzed using different kinetic models, including pseudo-first-order, pseudo-second-order, and intra-particle diffusion models, to elucidate the adsorption mechanism. The non-linear forms of these models were used to determine the rate constants and correlation coefficients. Lagergren's pseudo-first order equation is represented as Equation (7) (Su et al. 2020).

$$q_t = q_e(1 - e^{-k_1 t}) \quad (7)$$

where q_e (mg/g) and q_t (mg/g) are the amounts of adsorbate adsorbed at equilibrium and time t , respectively, and k_1 (min^{-1}) is the rate constant of pseudo-first-order adsorption. For the rate of

adsorption in the mechanism second-order, the pseudo-second-order kinetic velocity equation can be expressed as an Equation (8) (Ahmed et al. 2017):

$$q_t = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{t}{q_t}} \quad (8)$$

where k_2 ($\text{g g}^{-1} \text{min}^{-1}$) is the equilibrium rate constant of pseudo-second-order adsorption.

Intra-particle diffusion model

The intra-particle diffusion model is given by Equation (9) (Saha, Gayen, et al. 2023):

$$q_t = k_{id} t^{1/2} + C \quad (9)$$

Where q_t (mg/g) is the amount of adsorbate adsorbed at time t . k_{id} ($\text{mg/g/min}^{1/2}$) is the intra-particle diffusion rate constant. C is the intercept, which gives an idea about the boundary layer thickness.

Adsorption thermodynamics

To evaluate the adsorption thermodynamic of CSMB for BPS, the test was conducted at the conditions: initial BPS concentration = 150 ppm; pH, 6.0; adsorbent dosage, 0.7 g; contact time, 120 min in a 250 mL conical flask. The mixtures underwent agitation at 150 rpm, ranging from 298.15 K to 338.15 K in a temperature-controlled incubator shaker (Excelsa E24 Incubator shaker series, USA). The thermodynamic variables, including enthalpy change (ΔH), standard Gibbs free energy change (ΔG°), and change in entropy (ΔS°), were computed to understand the adsorption behavior of BPS on CSMB, and summarized using the following equations (Dawwam et al. 2022):

$$\Delta G_0 = -RT \ln K_L \quad (10)$$

$$K_L = \frac{q_e}{C_e} \quad (11)$$

$$\Delta S^\circ = \Delta H^\circ - \frac{\Delta G^\circ}{T} \quad (12)$$

Where ΔG° represents standard Gibbs free energy change, ΔS° signifies entropy change, ΔH° is the enthalpy change, R denotes the gas constant ($8.314 \text{ J/mol}^{-1} \text{K}^{-1}$), C_e is the equilibrium concentration of BPS (ppm), q_e is the quantity of BPS adsorbed onto biochar (mg/g), and T represents the absolute temperature (K).

Adsorbent regeneration study

To explore the regenerative capability of CSMB, the completely soaked CSMB (0.7 g) was treated separately using 0.1 M methanol as the elution medium at a concentration of 0.2 mol/L, and 150 ppm of the initial concentration of BPS was used for the regeneration test. The solution was agitated in 250 mL Erlenmeyer conical flasks using an orbital mixer overnight at 90 rpm. The desorption of adsorbed BPS was conducted over 2 h with continuous stirring at 160 rpm and ambient temperature (25 °C). Following this desorption process, the used CSMB was magnetically separated from the solution, and the spent CSMB was vacuum-dried at 40 °C for 24 h after that, and concentrations of BPS in the supernatant were analyzed to determine residual BPS concentrations, using a double-beam UV-visible spectrophotometer (Shimadzu UV-1800, Kyoto, Japan). Before commencing the next cycle, the CSMB was rinsed twice with distilled water after each removal cycle. The efficiency of BPS desorption from CSMB was evaluated using Equation (13) (Choi and Kan 2019).

$$\text{Desorption efficiency (\%)} = \frac{\text{Amount of BPS desorbed}}{\text{Amount of BPS adsorbed}} \times 100 \quad (13)$$

Results and discussions

Measurements of adsorbent

Analysis of a surface functional group of magnetic biochar before and after BPS adsorption

The fundamental chemical characteristics of CSMB, such as surface functional groups, play a crucial role in BPS adsorption. Minor peaks observed at 3286.6, 2340, and 1739.4 cm⁻¹ indicate the presence of residual O-H, C≡N, and C-O groups, respectively (Zhang et al. 2021). The peak observed at 3286.6 cm⁻¹ corresponds to the O-H stretching vibration of -OH (Guo et al. 2023), which appears broader and more robust in BPS due to hydrogen bonding between -OH groups. This signal indicates the presence of both unbound and intermolecularly bound hydroxyl groups, associated with the valence vibration of the hydrogen-bonded O-H group (Adeleke et al. 2024). Also, peaks at 1098.4 cm⁻¹ and

1220.6 cm⁻¹ correspond to the characteristic vibrations of -C=O and -C-O (Zhao et al. 2020), respectively. A novel peak at 649.4 cm⁻¹ confirms the presence of magnetite impregnation on the biochar surface (Li et al. 2020). The peaks observed in the adsorbent spectrum suggest the existence of surface functional groups capable of interacting with various adsorbates in the solution. Furthermore, Fe-O bonds indicate successful loading of Fe₃O₄ nanoparticles onto the biochar surface, as evidenced by SEM images. The assigned peak for the iron oxide compound aligns with findings from other studies (Feng et al. 2021; Li et al. 2020).

As depicted in Figure 2, the peaks corresponding to the magnetic biochar material appeared weaker than those of the CS biochar. Furthermore, after treatment, the magnetically loaded adsorbent showed reduced peaks assigned to hydroxyl groups. A new peak emerged in the spectra of the regenerated adsorbent within the 1400–1000 cm⁻¹ range, indicating the presence of BPS compounds (He et al. 2020).

Analysis of the crystal structure of the adsorbent

X-ray diffraction (XRD) analysis of an adsorbent material illustrates the nature and size of the planes of the produced material. Figure 3 shows the XRD spectrum of CSB and CSMB. The blue color representing CSB indicates the presence of characteristic broad peaks at low angles of amorphous charcoal, confirming that the

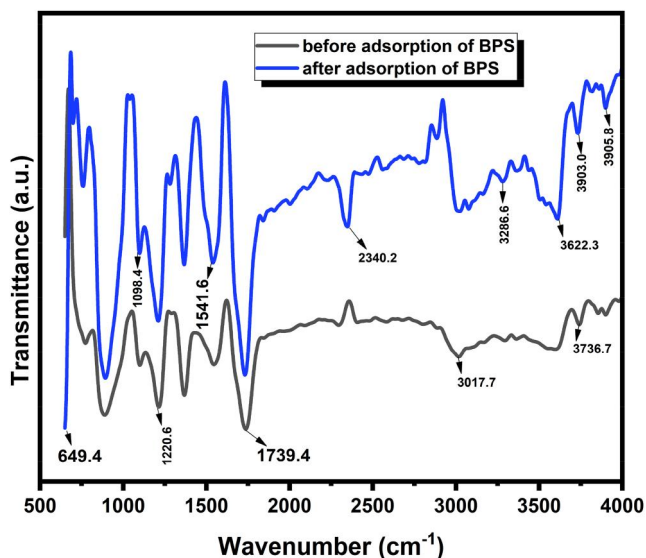


Figure 2. FT-IR spectrum studies of pristine and magnetic CSMB.

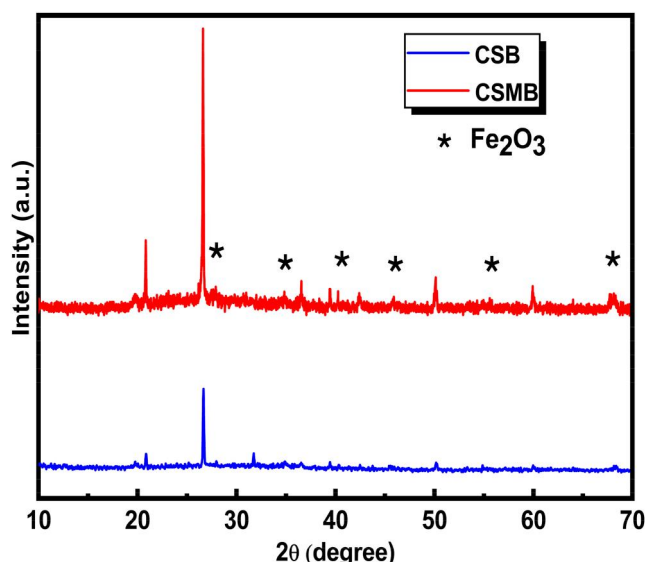


Figure 3. XRD pattern of the synthesized pristine CSB and CSMB.

amorphous structure of the biochar produced *via* pyrolysis lacks a well-defined crystalline structure. This indicates that the pristine CSB possesses a similar crystalline structure prior to magnetization. The absence of sharp peaks suggests that carbonization resulted in a disordered arrangement of carbon atoms, typical of biochar materials derived from biomass waste, including coconut shells.

Contrastingly, the XRD spectrum of CSMB, represented by the red color, exhibits additional sharp peaks superimposed on the broad background of the amorphous carbon structure. The appearance of distinct peaks at 30.4° , 35.8° , 38.5° , 43° , and 57.7° corresponds to the characteristic peaks of magnetite (Fe_3O_4) nanoparticles. These peaks indicate the successful loading of magnetic iron oxide species onto the biochar surface. These results are consistent with those observed by Zahedifar et al. (2021), in which peaks of magnetic biochar material emerged at 30.5° , 35.9° , 43.5° , 53.9° , 57.4° , and 63.0° . Fe_3O_4 nanoparticles on the CSMB surface imply that the magnetic treatment introduced a crystalline phase to the biochar, enhancing its magnetic properties and adsorption capabilities. This is consistent with prior studies that have shown the successful loading of magnetic iron oxide on biochar, as evidenced by the presence of strong and sharp peaks in the XRD spectrum (Katibi, Yunos, Man, Aris, Nor, Azis 2021; Nguyen et al. 2020; Shitu

et al. 2023). The XRD peak at approximately 43.28° corresponds to the graphite carbon in the biochar, indicating its formation (Tang et al. 2018). The comparison between the two spectra reveals a structural transformation from an amorphous CSB to a composite material with magnetic properties in CSMB. Incorporating iron species nanoparticles onto the biochar surface introduces crystallinity, forming additional adsorption sites and improving the efficiency of CSMB in removing BPS from aqueous solutions. The peak positions of these iron compounds are similar to those of previous investigations reported (Oyekanmi et al. 2024).

Morphological analysis of the adsorbent

Figure 4a-c shows FESEM images of neat and magnetic biochar before and after BPS adsorption. It can be noticed from Figure 4a that the neat CSB appear to be large block structures in different sizes prior to magnetic modification. The neat CSB shows quite a dense, rough surface with irregular pore distribution. Contrastingly, the morphology of CSMB in Figure 4b displayed a white and smooth chunked round-like layer structure. Moreover, CSMB exhibited a higher presence of minute pores than neat CSB. This alteration in morphology can be attributed to the activities of iron species nanoparticles on the biochar surface.

The morphological transformation revealed that magnetic treatment significantly transformed the structure of CSMB. More pores were developed on the CSMB surface, which exhibited clearly that iron species activation significantly changed the pore structure, which could result in producing more adsorption sites (Nguyen et al. 2021). The structural morphology of CSMB was considerably modified, probably rendering it an effective adsorbent. The CSMB adsorbent exhibits a multitude of crevices, voids, pores, ruptures, fractures, fissures, and indentations. These surface characteristics serve as active sites that enhance surface sorption. Furthermore, the elevated temperatures experienced during pyrolysis lead to the release of volatile substances within the microstructure of the particles. This phenomenon results in the formation of voids on the adsorbent's surface, eventually evolving into pores.

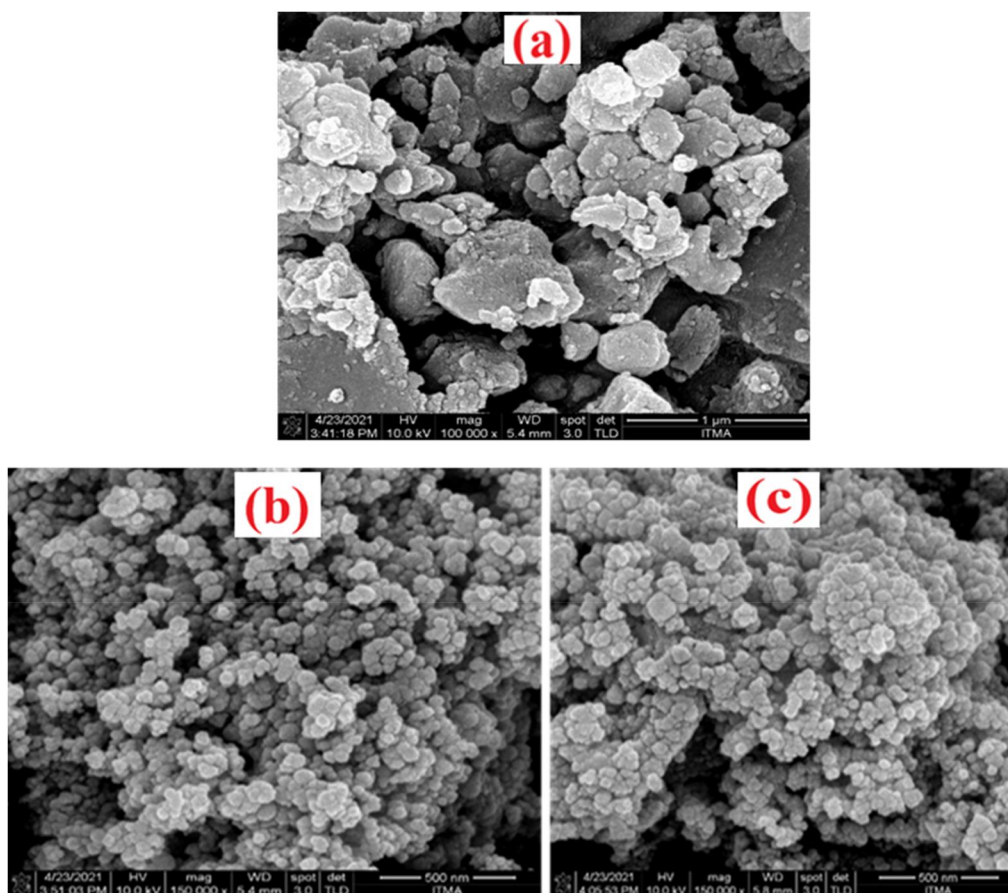


Figure 4. FESEM images of unmodified CSB (a), CSMB before BPS adsorption (b), and CSMB after adsorption.

Generally, such surface characteristics of the adsorbent create favorable conditions for the adsorption of different pollutants from water (Ighalo and Adeniyi 2020). The findings indicated that the magnetic biochar displayed a consistent distribution of Fe_3O_4 particles across its porous surface structure. SEM-EDX analysis (Figure 5) verified the presence of Fe species, with iron's atomic and weight ratio on the CSMB surface measured at 32.98%.

Elemental composition analysis

SEM-EDX obtained surface elemental compositions of CSMB. Oxygen, Carbon, Iron, Silicon, Nickel, and Nitrogen account for 43.36, 17.57, 32.98, 5.63, 0.22, and 0.24% weight percent for CSMB, respectively (Table 1). The summary of the physical properties and elemental composition of CSMB is presented in Table 1. The results indicated that CSMB was dominated by almost 43.36%O, and %Ni had the least amount (0.22%).

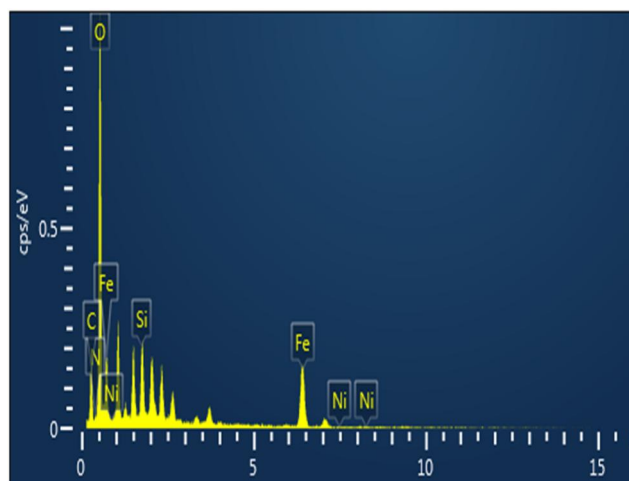


Figure 5. EDX spectra of the CS.

Furthermore, CSMB had a %Fe of 32.98%. This signifies that Fe_3O_4 could be the primary source of Fe. %C and %O of CSMB occupied 17.57% and 43.36%, respectively, which are likely to serve as functional groups on the surface of biochar. Figure 5 illustrates the EDX spectra of CSMB.

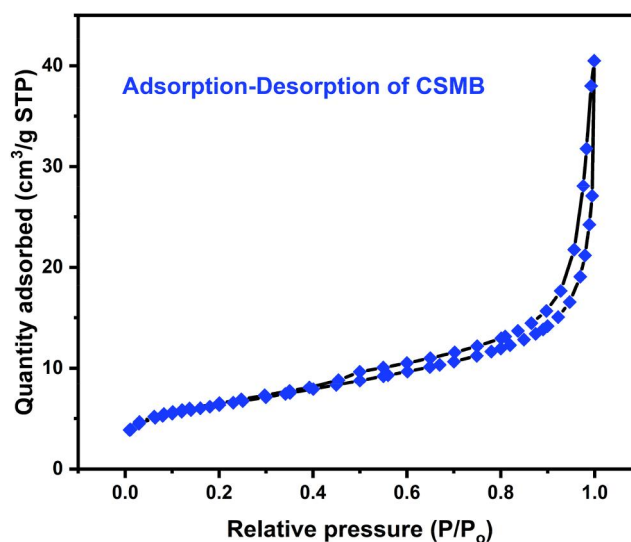
Table 1. Physical properties and elemental composition of CSMB.

Biochar samples	BET surface area (m ² /g)	Average pore diameter (Å)	C (wt.%)	O (wt.%)	Fe (wt.%)	Si (wt.%)	Ni (wt.%)	N (wt.%)
CSMB	373	19.75	17.57	43.36	32.98	5.63	0.22	0.24

The surface area together with the pore diameter of biochar are essential properties that influence adsorption and contaminants remediation (A. O. Adeleke et al. 2024; Iwar et al. 2021). It is noteworthy that superfluous surface area, as well as pore volume of biochar, play a prominent function in the adsorption of organic contaminants since they provide more active sorption sites, which enhance the adsorption capacity of organic molecules. The BET surface area of CSMB CS-based biochar is 373 m²/g with a mean pore diameter of 19.75 Å, as presented in Table 1, indicating its potential for effective adsorption. The high surface area of the CSMB biochar sample implies that it has a greater capacity to adsorb contaminants from water. Figure 6 illustrates the N₂ adsorption-desorption isotherms of CSMB at 77 K. The findings imply that the adsorption isotherm exhibited a relatively higher rise at relatively high relative pressures than comparatively low pressures. This indicates that the predominant adsorption occurs at moderately elevated pressures, indicating that the CS possesses high porosity with a narrow size distribution.

Analysis of surface charges of coconut shell magnetic biochar

The pH_{pzc} test was undertaken to analyze the surface properties (charges) of CSMB. The results indicated a pH_{pzc} value of 4.9 for CSMB, indicating that the surface of the sorbent possessed a net positive charge when the pH was below or equal to the pH_{pzc}, as well as a net negative charge when the pH was above the pH_{pzc} (Wang and Zhang 2020). Distinctively, CSMB showed a positively charged surface below the pH_{pzc} threshold, while pH levels above 4.9 rendered the surface negatively charged. Thus, the electrostatic interaction between the BPS anions and the CSMB occurred due to this charge difference. The pH_{pzc} value is more advantageous for the sorption of BPS anions, which usually occur in acidic solutions (Nguyen et al. 2021). The zeta potential of CSMB exhibited a consistent decrease with increasing pH, indicating that there is a

**Figure 6.** Nitrogen adsorption-desorption isotherm.

higher net negative surface charge at elevated pH levels. Likewise, the zeta potential of CSMB displayed both positive and negative values across the entire pH range examined (2–11), as depicted in Figure 7. Specifically, CSMB exhibited a positive charge when the pH was below 6.0. However, as the pH increased, the surface charge of CSMB transitioned rapidly from positive to negative. As pH steadily rises, CSMB's surface charges increase, and, observably, its zeta potential was −21.5 mV, which shows that CSMB was negatively charged (Figure 7).

Analysis of magnetic strength of coconut shell magnetic biochar

The magnetization curve of coconut shell magnetic biochar (CSMB) is shown in Figure 8. The saturation magnetization of the magnetic adsorbent, CSMB, was measured at 5.26 emu/g. This result indicates that the CSMB adsorbent possesses good magnetic properties, attributed to the incorporation of magnetic iron species within the biochar matrix, and the sorbent was easily recovered from the aqueous solution (Figure 8, inset). By exploiting the magnetic properties of the CS biochar, it can be efficiently recovered from aqueous solutions using an external magnet after the

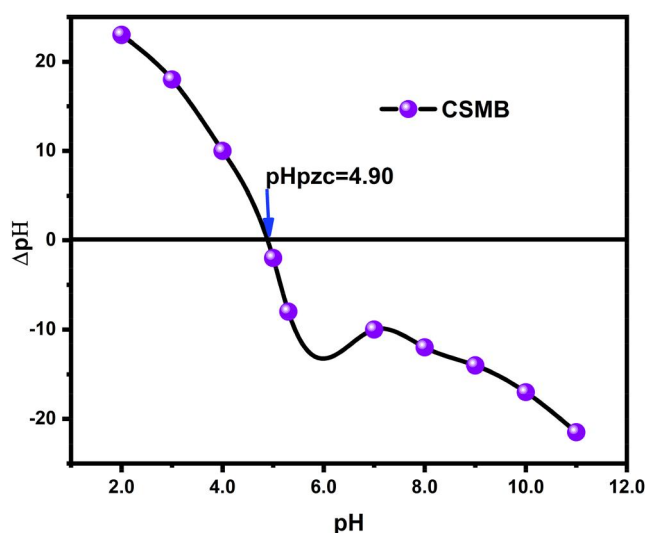


Figure 7. Zeta potential of CSMB under varying pH.

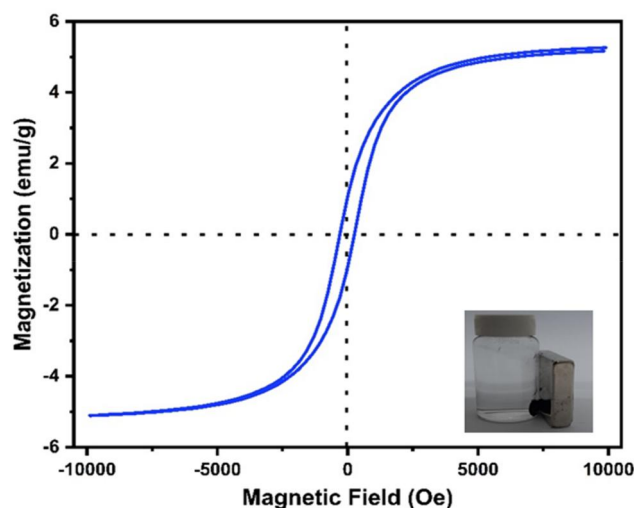


Figure 8. Magnetic hysteresis loop of CSMB.

adsorption process, thereby simplifying the separation and recovery process post-adsorption.

Adsorption test in an equilibrium condition

The adsorption capacity (q_e) and removal efficiency (R_e) for CSB and CSMB in the context of the BPS adsorption test in equilibrium conditions. The volume, initial concentration, pH, time, and mass are kept constant to observe the removal of BPS and adsorption capacity. CSMB exhibited a higher removal efficiency (94.3%) than CSB (81.47%) as shown in Figure 9. This indicates that CSMB is more effective at removing BPS from the solution. CSMB also showed a higher adsorption capacity (43.5 mg/g) than CSB (26.7 mg/g) (Figure 9). This means that CSMB

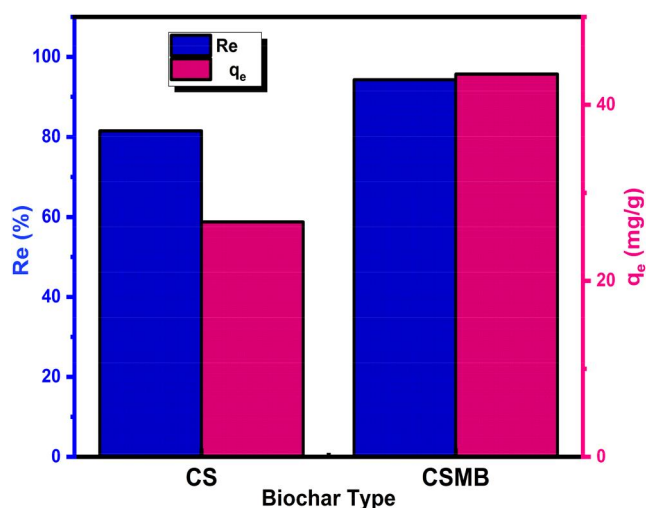


Figure 9. Adsorption capacity and removal of BPS at equilibrium (BPS: 150 ppm; pH: 6.0, agitation speed: 300 rpm, dosage: 0.7 g temperature: 25 °C).

can adsorb a more significant amount of BPS per unit weight of biochar compared to CSB. The results suggest that CSMB is more effective in removing BPS from the solution than non-modified biochar (CSB). CSMB achieved a higher percentage of BPS removal and exhibited a greater adsorption capacity, indicating its potential as an effective adsorbent for BPS in water treatment or purification processes.

Batch adsorption studies

Effect of adsorption operating variables on the removal of BPS in aqueous solution

Effect of contact time on BPS adsorption capacity.

Contact time significantly impacts the cost-efficiency and economic advantages of any treatment method. In this study, we investigated the impact of contact time on BPS removal rate. The contact time was experimentally examined between 30 and 150 min. Figure 10 illustrates the effect of contact time on the adsorption capacity of BPS using CSMB. The adsorption capacity was evaluated at various time intervals ranging from 0 to 150 min. The results reveal a dynamic adsorption process characterized by an initial rapid uptake of BPS followed by a gradual approach to equilibrium. At the initial contact time of 0 min, the adsorption capacity is 14.84 mg/g, indicating the inherent affinity of CSMB for BPS. As the contact time increases to 30 min, the adsorption capacity rises sharply to 22.61 mg/g. This rapid increase

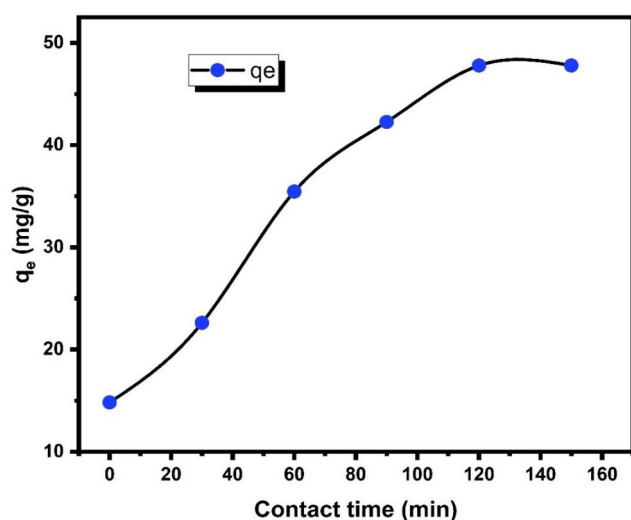


Figure 10. Effect of contact time on BPS adsorption capacity (BPS: 20 ppm; pH: 6.0, agitation speed: 300 rpm, dosage: 0.7 g temperature: 25 °C).

continues, reaching 35.46 mg/g at 60 min and 42.27 mg/g at 90 min. The initial rapid phase of adsorption can be attributed to the high availability of active sites on the surface of CSMB, which facilitates the swift capture of BPS molecules from the aqueous solution.

The adsorption capacity further increases to 47.79 mg/g at 120 min. However, beyond this point, the rate of increase diminishes, and the adsorption capacity plateaus, remaining approximately 47.79 mg/g at 150 min. This plateau signifies that the adsorption sites on CSMB are approaching saturation, and the system is reaching equilibrium, due to the sorption sites having been drenched on the sorbent surface since it becomes difficult for BPS molecules to find more available sorption sites for adsorption (Zhang et al. 2022). The equilibrium condition, where no significant increase in adsorption capacity is observed despite the extension of contact time, suggests that the maximum adsorption capacity of CSMB for BPS under the given experimental conditions is approximately 47.79 mg/g. This equilibrium state is a critical factor in adsorption studies as it defines the optimal contact time required for maximum pollutant removal efficiency.

From a kinetic perspective, the rapid initial phase likely follows a pseudo-second-order kinetic model, which assumes that the adsorption rate is proportional to the square of the number of unoccupied sites. This model is often indicative of

chemisorption, where the adsorption involves the formation of chemical bonds between the BPS molecules and the active sites on the CSMB. The gradual approach to equilibrium further supports the notion of a strong interaction between the adsorbent and the adsorbate.

Prolonging the contact time beyond the equilibrium point does not enhance adsorption capacity and may lead to inefficiencies in the process (Iwar et al. 2021; Katibi et al. 2024). Therefore, identifying the equilibrium time is essential for maximizing adsorption efficiency while minimizing operational costs. Moreover, the high adsorption capacity observed in this study highlights the efficacy of CSMB as an adsorbent for BPS removal from aqueous solutions. The results suggest that CSMB can be effectively utilized in water treatment processes to address the contamination of water bodies by endocrine-disrupting compounds such as BPS. Hence, the study of contact time effects on BPS adsorption capacity by CSMB demonstrates a clear trend of initial rapid adsorption followed by a plateau at equilibrium. This understanding is crucial for the practical implementation of adsorption-based water treatment technologies, ensuring that the processes are both efficient and cost-effective.

Effect of pH on BPS adsorption capacity. The influence of solution pH on BPS adsorption capacity using CSMB adsorbent is critical to understanding environmental remediation processes. Figure 11 shows how changes in solution pH influence the adsorption capacity of BPS onto the CSMB sorbent. The interface between the adsorbate as well as adsorbent is primarily influenced by the solution's pH (Iwar et al. 2021; Sulaiman et al. 2021). Figure 10 illustrates the relationship between the adsorption capacity of BPS and the solution pH, ranging between 3.0 and 11.0. As the pH increases from 3.0, the adsorption capacity sharply rises until reaching pH 6.0, where the maximum adsorption capacity is achieved at pH 6.0 (52.3 mg/g). However, beyond pH 6.0, the adsorption capacity starts to decline. At pH 7.0 and 8.0, there is a noticeable decline in BPS adsorption capacity, indicating that the adsorption process becomes less efficient under neutral to slightly acidic conditions. This decline

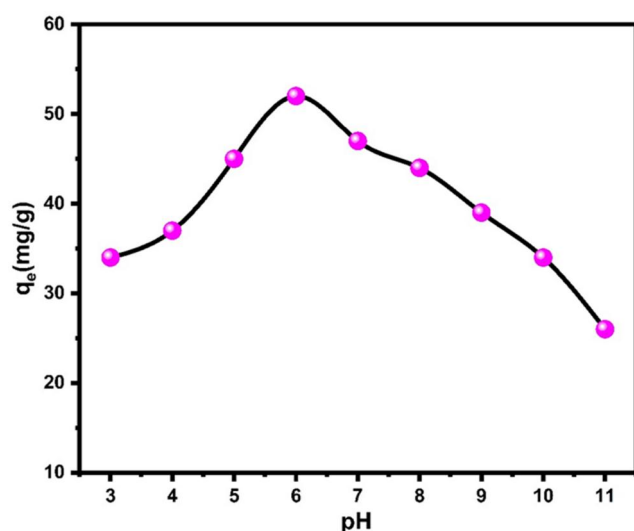


Figure 11. Effect of pH on the adsorption of BPS using CSMB (BPS = 20 ppm; temperature: 25 °C; dosage: 0.7 g; agitation speed: 300 rpm).

continues as the pH level becomes more basic, with the lowest adsorption capacity recorded at pH 11.0, where only 26 mg/g of BPS is adsorbed, indicating that the adsorption process is less favorable or less efficient under basic (alkaline) conditions. This decline in adsorption capacity suggests that the adsorbent's surface properties or the adsorbate's chemical nature may be less conducive to adsorption at higher pH levels. The observed pattern can be ascribed to the charge characteristics of both BPS and the CSMB adsorbent at different pH levels.

At lower pH values (acidic conditions), the surface of the biochar sorbent may become positively charged, while BPS tends to be more negatively charged. This electrostatic interaction between the adsorbent and the pollutant reduces adsorption capacity. Conversely, at slightly alkaline conditions (pH 6.0), the surface charge of the adsorbent may favorably interact with BPS molecules, leading to enhanced adsorption. Similar findings were reported by (Li et al. 2020; Wang and Zhang 2020), where maximum BPA adsorption occurred at pH 6.0 pomelo peel magnetic biochar and composite material of CoFe_2O_4 -biochar. At lower pH levels, the protonation of surface-active sites and abundance of H^+ ions results in a positively charged biochar surface, leading to electric repulsion between cationic BPS and CSMB. Conversely, at higher pH levels, the deprotonation of active sites renders

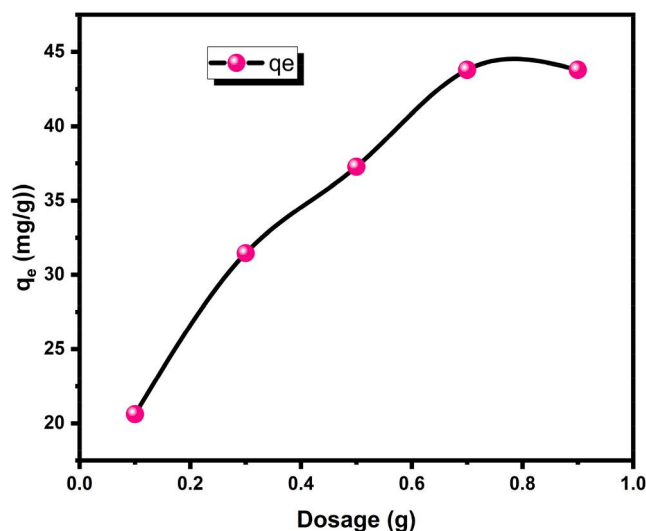


Figure 12. Effects of CSMB dosage on BPS adsorption capacity (BPS: 20 ppm; pH: 6.0, agitation speed: 300 rpm, temperature: 25 °C).

the CSMB surface negatively charged, facilitating electrostatic attraction between the CSMB surface and BPS anions molecules. Thus, the results indicate that solution pH significantly influences BPS adsorption onto magnetic biochar adsorbents.

Effect of magnetic biochar dosage on BPS removal and adsorption capacity

Figure 12 illustrates the effects of varying dosages of CSMB on the adsorption capacity of BPS. The results show a gradual increase in adsorption capacity with increasing dosages of CSMB, highlighting the relationship between adsorbent amount and pollutant adsorption capacity. At a dosage of 0.1 g, the adsorption capacity is 20.61 mg/g. As the dosage increases to 0.3, 0.5, and 0.7 g, the adsorption capacity correspondingly rises to 31.46 mg/g, 37.27 mg/g, and 43.79 mg/g, respectively. This trend indicates that more active sites are available for BPS molecules with higher dosages, thereby enhancing the adsorption process. However, beyond a dosage of 0.7 g, the adsorption capacity attains a plateau, with a maximum recorded value of 43.79 mg/g at both 0.7 and 0.9 g dosages. This phase indicates that the adsorption sites on the CSMB are saturated at higher dosages, and additional biochar does not contribute to further adsorption. The equilibrium condition is achieved at this point, where no significant increase in adsorption capacity is observed despite the increase in adsorbent

dosage. The equilibrium condition indicates the maximum adsorption capacity of CSMB for BPS under the given experimental conditions is approximately 43.79 mg/g. This saturation effect can be attributed to the limited availability of active sites, which, once occupied, cannot accommodate further BPS molecules. It implies that at higher dosages, the excess biochar remains unutilized, leading to no further improvement in adsorption efficiency.

Hence, understanding this equilibrium condition is crucial for practical applications. It helps in determining the optimal dosage of CSMB required to achieve maximum adsorption efficiency without wastage of the adsorbent material. This insight is valuable for scaling up the adsorption process for industrial applications, ensuring both cost-effectiveness and efficient pollutant removal. Also, after equilibrium is attained, fewer active sorption sites exist, which causes a lower removal rate and quantity adsorbed. Besides, higher adsorbent dosage could result in adsorbent particle accretion which will lead to limited active binding sites (Adeleke et al. 2024; Scaria et al. 2022). Hence, the result shows that increasing the CSMB dosage in the solution positively affects both the adsorption capacity and the remediation of BPS.

Effect of initial concentration on BPS removal.

Figure 13 shows the effect of initial BPS concentration on the adsorption capacity of CSMB. The results demonstrate a clear trend: the adsorption capacity of CSMB increases significantly with higher initial concentrations of BPS. At an initial BPS concentration of 8 mg/L, the adsorption capacity is 14.61 mg/g. As the initial concentration increases to 25 mg/L, 50 mg/L, and 100 mg/L, the adsorption capacity correspondingly rises to 26.46 mg/g, 35.27 mg/g, and 40.79 mg/g, respectively. This increasing trend indicates that higher initial concentrations of BPS enhance the adsorption capacity due to the greater availability of BPS molecules, which stimulates more frequent interactions between the BPS molecules and the active sites on the CSMB. At the highest tested concentration of 150 mg/L, the adsorption capacity further increases to 47.79 mg/g. This continuous rise in adsorption capacity implies that

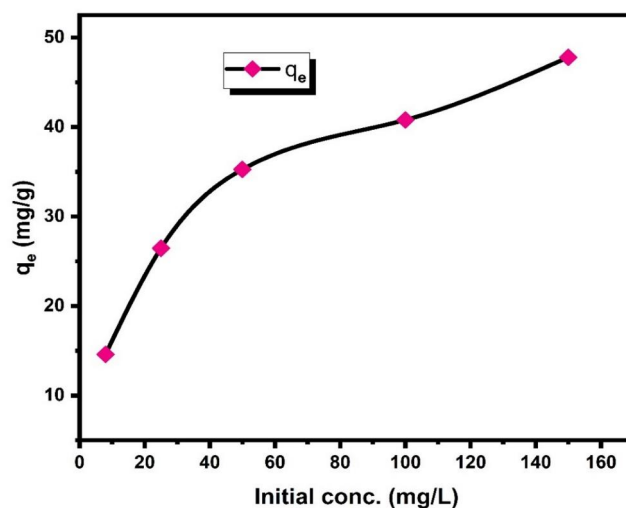


Figure 13. Effect of initial concentration on BPS adsorption capacity (pH: 7.0, agitation speed: 300 rpm, dosage: 0.7 g; temperature: 25 °C, and reaction temperatures (298.15 K).

the adsorption process is strongly dependent on the initial concentration of BPS. Higher concentrations provide a greater driving force for mass transfer, facilitating faster diffusion of BPS molecules toward the active sites on the CSMB, thus leading to higher uptake.

The results can be attributed to the mass transfer effect, where a higher initial concentration provides a steeper concentration gradient. This gradient enhances the driving force for the diffusion of BPS molecules to the CSMB's surface, resulting in increased adsorption. The findings highlight that no saturation point was reached within the tested concentration range, indicating the high adsorption potential of CSMB for BPS.

BPS sorption isotherm study

Adsorption isotherms are described about equilibrium adsorption capacity as well as the concentration of the solution. Herein, we essentially studied the adsorption isotherms of CSMB. Isothermal adsorption models including Freundlich and Langmuir, were employed to describe adsorption capacity. As previously mentioned, many models were utilized to correlate the adsorption capacity and residual adsorbate concentration, including Langmuir and Freundlich.

Freundlich isotherm

For the Freundlich model, the exponent (n) is 0.5017, which characterizes the adsorption

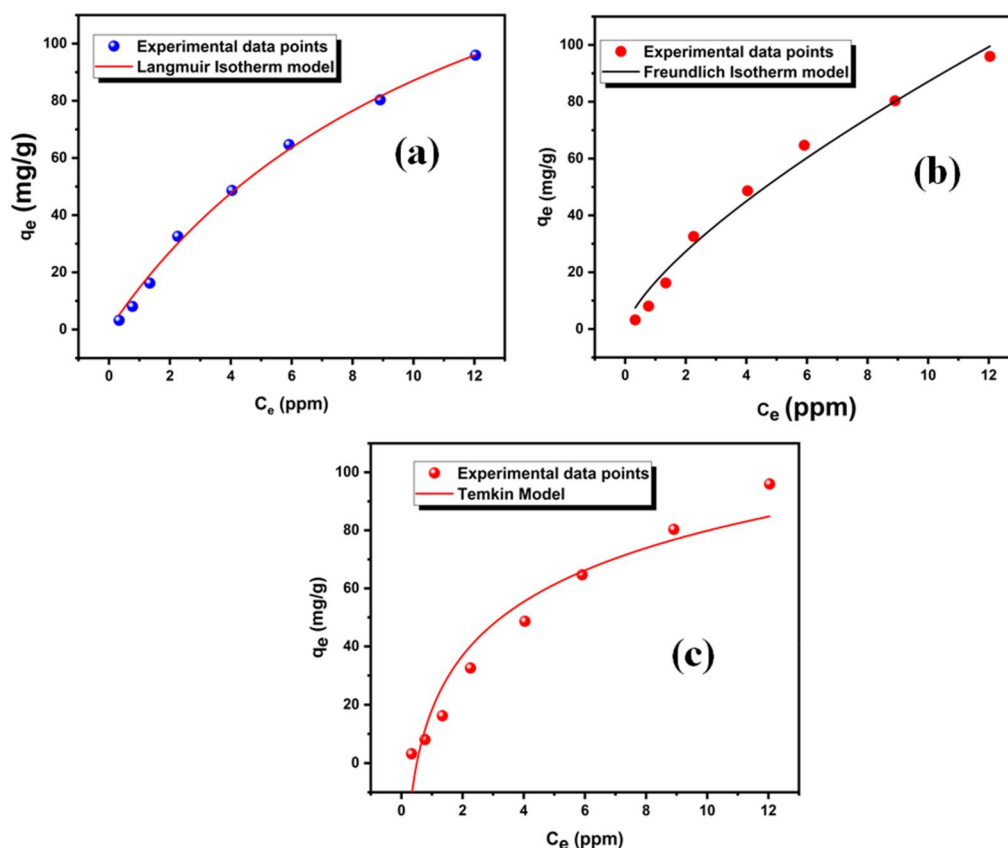


Figure 14. Freundlich isotherm model (a), Langmuir isotherm model (b) Temkin isotherm model (c).

intensity or surface heterogeneity. Values of n between 0 and 1 suggest favorable adsorption. The coefficient of determination (R^2) for the Freundlich model is 0.98493 as shown in (Figure 14a), implying that the model and the data are well-fitted. The Freundlich model suggests favorable adsorption with moderate adsorption intensity. These findings are valuable for understanding the adsorption behavior of the CSMB and its potential applications in removing substances from solutions.

Langmuir isotherm

The coefficient of determination (R^2) was 0.99385 for the Langmuir isotherm (Figure 14b), which indicates the applicability of this model in illustrating the adsorption data. When the R_L value ranges from 0 to 1, adsorption of a pollutant is deemed advantageous; conversely, it is classified as disadvantageous for R_L values exceeding 1, irreversible for R_L equal to 0, and linear for R_L equal to 1. In the present study, the measured R_L value (0.153) signifies the favorable adsorption of BPS onto CSMB.

Temkin isotherm

The Temkin isotherm model is used to describe the adsorption of Bisphenol S (BPS) onto CSMB adsorbent, understanding the adsorption process involving interactions between the adsorbent and adsorbate. The model's (R^2) value of 0.93304, while indicating a reasonable fit, is lower than those of the Langmuir and Freundlich models, suggesting that the Temkin model is less suitable for describing this adsorption process. The Temkin constants (A) and (B), which are 1.98602 and 26.72287, respectively, provide information on the binding energy and the heat of adsorption. The relatively high value of (B) implies significant interaction between the adsorbent and adsorbate, suggesting that adsorption energy decreases linearly with surface coverage due to adsorbate-adsorbate interactions. However, with the lower (R^2) value compared to the other models, it can be inferred that the adsorption of BPS onto CSMB is influenced more by factors explained in the Langmuir and Freundlich models, such as monolayer adsorption on a homogeneous surface and heterogeneous surface adsorption, rather than by the assumptions of the Temkin model.

Table 2. Adsorption isotherms variables.

Adsorbent	Langmuir model				Freundlich model				Temkin model		
	$q_{\max}$ (mg/g)	K_L (L mg ⁻¹)	R^2	R_L	n	$1/n$	R^2	K_F (L mg ⁻¹)	A	B	R^2
CSMB	48.7	4.27403	0.99385	0.00615	0.5017	1.9931	0.98493	21.7	1.98602	26.72287	0.93304

Table 2 presents the adsorption isotherm variables for a CSMB, demonstrating the fitting of Langmuir as well as Freundlich models. Table 2 indicates that the optimum monolayer adsorption capacity of the adsorbent is found to be 48.7 mg/g. This value represents the maximum amount of adsorbate (BPS) that the adsorbent can hold onto its surface. The computed Langmuir constant K_L is 4.27403 L mg⁻¹. This constant provides information about the energy of adsorption; higher values indicate stronger adsorption. The coefficient of determination (R^2) is 0.99385 as illustrated in (Figure 14b), which is very close to 1. This indicates that the Langmuir model provides an excellent fit to the data. The separation factor (R_L) was calculated to evaluate the favourability of the adsorption process. This suggests that the synthesized biochar has a high potential for removing BPS from aqueous solutions. The computed separation factor R_L is 0.00615 for all initial concentrations of BPS, which indicates favorable adsorption as R_L is between 0 and 1. The closer R_L is to zero, the more favorable the adsorption.

Evidently, the data on adsorption exhibit a strong alignment with the Langmuir isotherm model, as indicated by the notably high coefficient of determination (R^2) of 0.99385 (Figure 14b). This indicates an outstanding fit between the investigational data and the model. In this case, the Langmuir model provides an almost ideal description of the adsorption behavior of the CSMB for BPS (adsorbate) under the given conditions. The Langmuir model presumes that adsorption occurs as a monolayer on the adsorbent's surface, where each adsorbate molecule occupies a specific site. The high R^2 value suggests that the adsorption of the substance onto the CSMB follows a monolayer adsorption process. The computed $q_{\max}$ value of 48.69 mg/g indicates that the CSMB has a significant adsorption capacity for the BPS. This quantity denotes the maximum adsorbate capacity per unit mass of the CSMB. The computed separation factor R_L , at 0.00615, lies within the 0 to 1 range, signifying favorable adsorption. A

value of R_L approaching zero implies significantly favorable adsorption. Put differently; the Langmuir model proposes that the adsorption of BPS compound onto the CSMB is both favorable and effective.

Every adsorption site on the CSMB is presumed to be comparable by the Langmuir model since it shows a homogenous surface. The model's good fit implies that the biochar's surface has uniform adsorption sites for the BPS adsorbate. Hence, the alignment of the adsorption data with the Langmuir model signifies that the adsorption of the BPS substance onto the CSMB follows a monolayer adsorption process, is highly favorable, and occurs on a surface with uniform and equivalent adsorption sites. This information is valuable for water treatment and pollutant removal applications, where a high adsorption capacity and efficiency are desirable.

Adsorption kinetics

The study of adsorption kinetics plays a critical role in evaluating the adsorption capability of an adsorbent (Iwar et al. 2021; Kameda et al. 2019). The pseudo-first-order and pseudo-second-order models were used to analyze the kinetics data. The resulting correlation coefficients (R^2) were utilized to evaluate the suitability of the kinetic models (Katibi et al. 2021). The linearized plots are shown in Figures 15a and 15b, and the values of k_1 , k_2 , Q_e , and R^2 were also computed and presented in Table 3. Figure 15 demonstrates the impact of contact duration on the adsorption capacity of CSMB for BPS. The duration of contact between the adsorbate and adsorbent plays an essential role in estimating the duration of adsorption until equilibrium is reached. To investigate this, a series of batch kinetic experiments were conducted, with contact durations ranging from 10 to 180 min for the removal of BPS. Figures 15a and 15b show that the removal of the BPS increased gradually during the adsorption period up to 180 min. As the reaction time increased, BPS adsorption amounts rose rapidly.

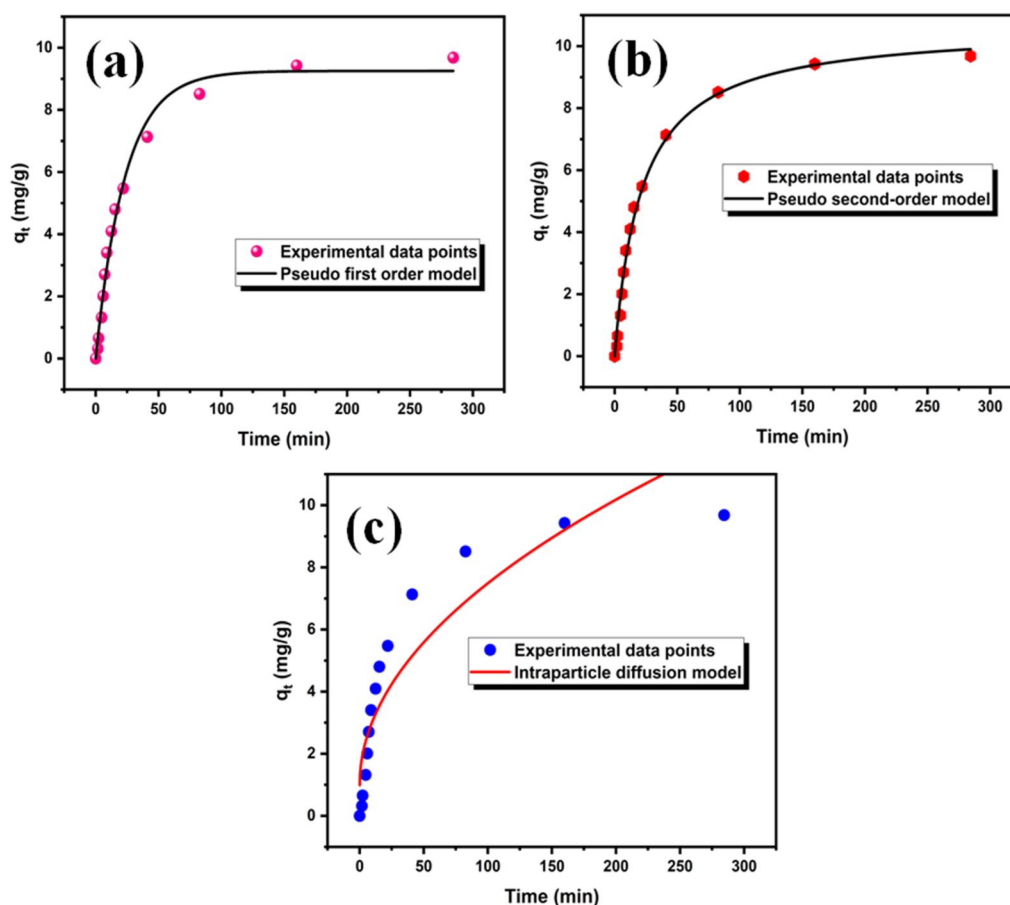


Figure 15. Adsorption kinetic of BPS fitted by pseudo first-order(a), pseudo second-order (b), and intra-particle diffusion (c).

Table 3. Kinetic model parameters for BPS removal.

Kinetic model	Parameters	BPS
Pseudo-first order	$q_{e, \text{exp}}$ (mg/g)	43.5
	$q_{e, \text{cal}}$ (mg/g)	57.53
	$K_1 \text{ min}^{-1}$	0.01175
	R^2	0.98919
Pseudo-second-order	$q_{e, \text{exp}}$ (mg/g)	43.5
	$q_{e, \text{cal}}$ (mg/g)	49.48
	$K_2 \text{ (g mg}^{-1} \text{ min.}^{-1})$	5.47
	R^2	0.99196
Intraparticle diffusion	$K_{id} \text{ (mg/g} \cdot \text{min}^{0.5})$	0.64989
	C	0.98888
	R^2	0.84514

The experimental values closely aligned with computed PSO model values for BPS removal when compared to the fitted experimental data of the PFO kinetic model.

The Intraparticle diffusion model assesses whether the adsorption process is influenced by the diffusion of adsorbate molecules within the pores of the adsorbent. The R^2 value of 0.84514 is lower than the PFO and PSO models, indicating a less satisfactory fit. The intercept C of 0.98888 implies that intraparticle diffusion is not the sole rate-controlling step and that there may

be other contributing mechanisms, such as boundary layer diffusion. The lower R^2 value also indicates that while intraparticle diffusion plays a role in adsorption, it is not the dominant mechanism. Hence, a comparison between the PFO model, PSO model, and intraparticle diffusion model revealed that the PSO model yielded a superior R^2 value (approximately 0.99196), indicating a better fit for the adsorption of BPS by CSMB compared to the PFO model with R^2 (0.98949) and intraparticle diffusion model with R^2 (0.84514). For BPS, the best fit of the experimental result fitted to the PSO model achieved the highest R^2 value of 0.99196 (Table 3), indicating that the adsorption of the BPS on CSMB was *via* chemisorption. Apart from high correlation value, the PSO exhibited high proximity between the experimental uptake capacity (q_e (exp)) (46.15 mg/g) and the calculated uptake capacity (q_e (cal)) (51.37 mg/g), indicating that the adsorption of BPS onto CSMB was regulated by chemisorption.

Table 4. Computed thermodynamic variables for BPS adsorption onto CSMB at varying temperatures.

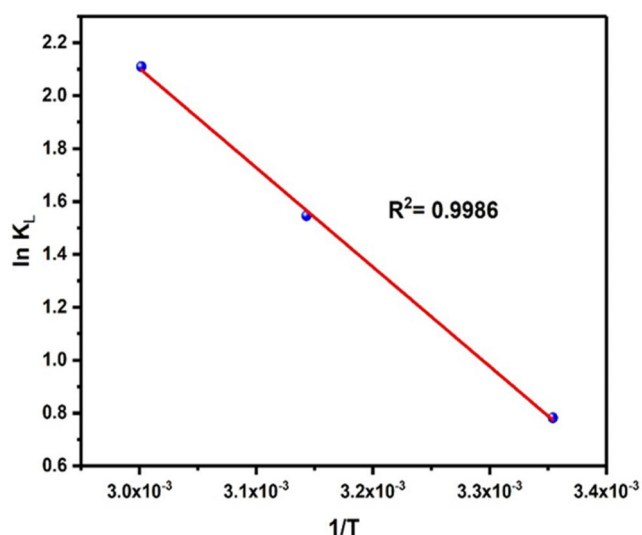
Temperature (K)	$\ln K_L$	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol·K)
298.15	0.78	−1.94	31.22	111.14
318.15	1.55	−4.09		
333.15	2.20	−5.84		

Thermodynamic studies

Table 4 presents the calculated thermodynamic parameters of the adsorption of BPS on CSMB across different temperature conditions. These parameters play a crucial role in elucidating the spontaneity and energetics associated with the adsorption phenomenon. The graphical representation of the natural logarithm of the distribution coefficient, $\ln K_L$, was depicted in Figure 16 with respect to the reciprocal of temperature, $1/T$, to elucidate the impact of temperature variation on the process of adsorption. It was observed that the $\ln K_L$ values exhibit an upward trend as temperature increases. This observation suggests that the adsorption phenomenon manifests greater favourability at elevated temperatures. The positive nature of these values signifies the endothermic aspect of the adsorption process, thus implying a consumption of heat energy. Conversely, the consistently negative standard Gibbs free energy change, ΔG° , across all temperature points indicates that the adsorption of BPS onto CSMB biosorbent follows a spontaneous course.

Furthermore, the progressively more negative trends observed at elevated temperatures suggest a heightened spontaneity in the adsorption mechanism as temperature increases. The positive standard enthalpy change (ΔH°) signifies an endothermic adsorption process, indicating heat absorption from the surroundings. This suggests that the affinity of BPS for CSMB is enhanced at higher temperatures due to the increased heat absorption, as depicted in Figure 16. The positive standard entropy change (ΔS°) values indicate a rise in randomness or disorderliness during adsorption. This implies that the adsorption of BPS onto CSMB results in amplified disorder at a molecular level, a common occurrence in physical adsorption phenomena.

Hence, the results indicate that BPS adsorption onto CSMB is an unconstrained and endothermic process preferred at higher temperatures. These findings provide valuable insights into the

**Figure 16.** Thermodynamic plot (pH: 7.0, dosage: 0.7 g; agitation speed: 300 rpm; BPS: 150 ppm).

feasibility and energy requirements of using CSMB for BPS removal in wastewater treatment or other environmental applications.

Adsorbent regeneration study

The reusability of the CSMB was assessed by subjecting it to five consecutive cycles at room temperature to confirm its effectiveness as an adsorbent. The CSMB sorbent was reused five times at ambient temperature to assess the reusability of the adsorbent. The findings revealed a slight decline in efficiency from 98.51% after five cycles to approximately 89%. This decline could be attributed to the leakage of active sites into the BPS ions and the blockage of active sites by sorbent materials. The result demonstrates superior recyclability compared to alternative sorbents (Rong et al. 2019; Yin et al. 2022; Zhang et al. 2020). Figure 17 illustrates the sorbent's recyclability for BPS adsorption until five cycles. As noticed in Figure 17, the adsorption efficiency of the adsorbent declines after the first cycle, and then an insignificant loss of adsorption capacity is noticed. The results indicated that CSMB could be regenerated and utilized repetitively in water treatment.

Possible removal mechanism

Understanding the adsorption mechanism of magnetic biochar is essential for its effective application in water treatment (Saha et al. 2024).

Figure 18 illustrates the various mechanisms involved in the adsorption of BPS onto CSMB, such as surface complexation, electrostatic attraction, chemical precipitation, coordination reactions, ion exchange, and hydrogen bonding. These mechanisms are influenced by the functional groups, pore structure, and chemical bonds present on the surface of the CSMB. Research has shown that major mechanisms for BPS adsorption include pore-filling effects, hydrophobic interactions, electrostatic attraction, chemical reduction, hydrogen bonding, electron transfer,

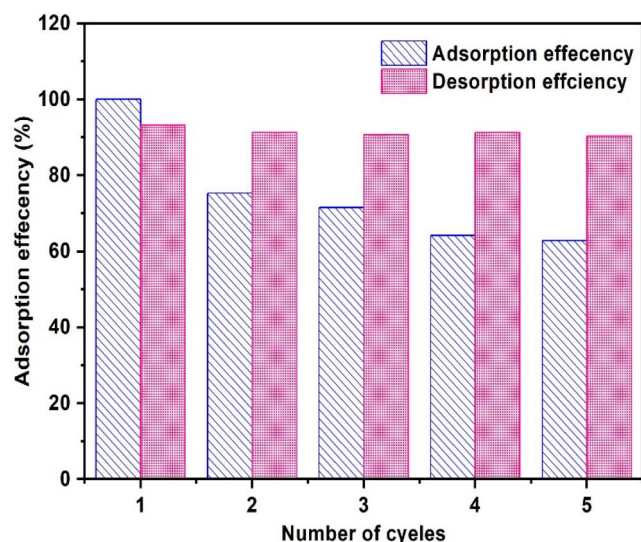


Figure 17. Reusability of CSMB for adsorption of BPS from aqueous solution (pH: 6.0; dosage: 0.7 g; agitation speed: 300 rpm; BPS: 150 ppm).

surface complexation, and π - π interactions (Katibi et al. 2024). Electrostatic interaction plays a significant role in BPS adsorption by carbon materials, while pore-filling involves the adsorbate entering the pores of the porous adsorbent (Yi et al. 2019). Rong et al. (2019) Prepared magnetic biochar from banana peels for BPA adsorption, highlighting its large specific surface areas, rich micropores, and superior crystallinity. These properties align with the microporous filling effects, enhancing BPS adsorption. Also, the high adsorption capacity of BPS was linked to the pore volume of the magnetic biochar, confirming the significant role of pore-filling in BPS uptake (Ahmed et al. 2018). The formation of hydrogen bonds is common in many adsorption processes, and electron transfer also occurs during the adsorption of organic contaminants.

Economic assessment

The cost of adsorbents significantly influences the cost-effectiveness of a water treatment facility. Several factors affect the cost of adsorbent materials, including their availability, treatment, and process requirements (Saha, Gayen, et al. 2023). The economic viability of using coconut shell magnetic biochar (CSMB) for BPS sequestration is critical to its potential large-scale application. This assessment includes an analysis of raw material costs,

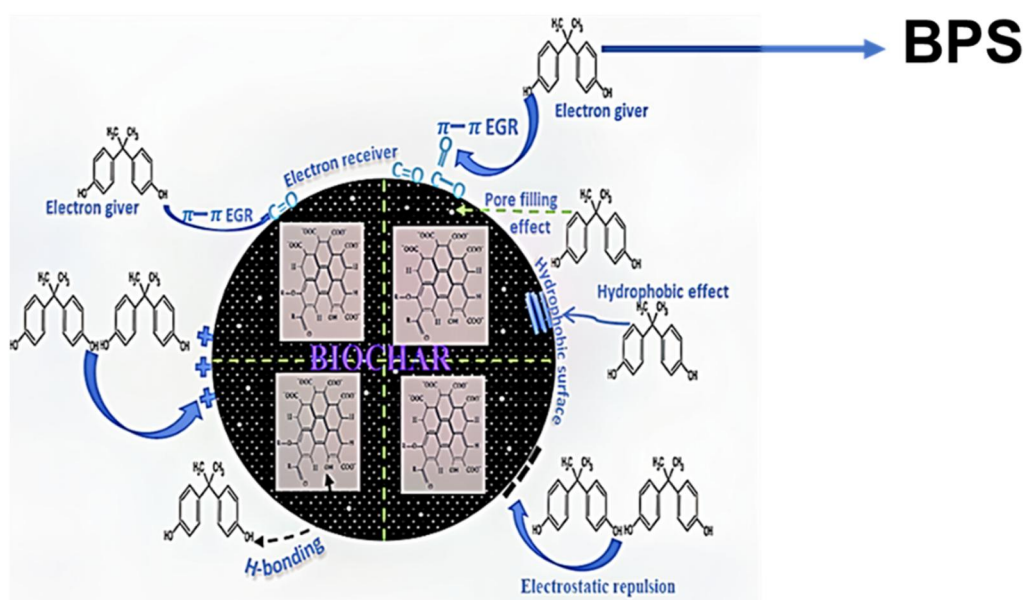


Figure 18. Possible BPS removal mechanism using CSMB.

production costs, operational costs, and potential savings from the reuse of CSMB. It also involves compiling the materials used with the manufacturer's unit prices. The cost estimation presented in Table 5 outlines the expenses associated with producing coconut shell magnetic biochar (CSMB) and utilizing it for water treatment. The raw material costs for the coconut shells are minimal, as they are obtained free of charge and processed manually without any significant expense. The required chemicals, including iron sulfate, iron chloride, and sodium hydroxide, contribute to a modest total cost of 23.28 MYR. The processing costs, which encompass the pyrolysis process and magnetic stirring, amount to 120 MYR. Including an additional 10% of the total cost to account for incidental expenses, the overall cost of producing CSMB is 158.37 MYR, equivalent to approximately 36.43 USD.

Considering the cost covers the production of 10 kg of CSMB, the cost per kg would be around 3.64 USD. Thus, the study demonstrates a relatively low total cost, comparable to previously reported prices for other biochar adsorbents, which ranged from \$0.56 to \$5.49 per kg (Chakraborty et al. 2018; Isaac and Siddiqui 2022; Isaac et al. 2023; Norberto et al. 2023). Hence, this cost-effectiveness revealed the potential of CSMB as an affordable and efficient option for water treatment applications.

Performance evaluation of CSMB adsorption capacity for BPS uptake

To evaluate the performance of CSMB in removing BPS from aqueous solutions, a comparative study was conducted against other magnetic biochar adsorbents. The adsorption capacity of CSMB was assessed under optimal conditions and compared with the adsorption capacities of other magnetic biochars reported in the literature. The batch adsorption tests revealed that the adsorption capacity of CSMB for BPS was 52.3 mg/g under optimal conditions (pH 6, contact time of 150 min, and temperature of 298.15 K).

In comparison with other magnetic biochar adsorbents, CSMB demonstrated superior performance. For instance, magnetic pine sawdust Biochar

Table 5. Cost estimation.

Raw material/chemicals	Sub section	Quantity	Cost break up (MYR)	Total cost (MYR)
Coconut Shells production	Collection of raw feedstock Size reduction Washing cost	1 kg	Raw coconut waste was obtained free of cost Done manually Distilled water from the research lab	0.00 0.00 0.00
Total				0.00
Chemicals required	Iron Sulfate Iron Chloride Sodium Hydroxide Water	2 g 2 g 4 g 500 L	0.208 MYR/kg 0.144 MYR/kg 5.82 MYR/kg Distilled water obtained from the laboratory hour $\times$ unit $\times$ Unit cost = $2 \times 2 \times 7.50$ hours $\times$ unit $\times$ per unit cost = $6 \times 2 \times 7.50$	0.416 0.288 23.28 30 90 143.98 14.39 158.37
Magnetic biochar processing	Pyrolysis Process cost Magnetic stirring cost			
Total Cost				
10 % of total cost				
Overall Cost				158.37

derived from sawdust showed an adsorption capacity of 13.83 mg/g (Reguyal et al. 2017), while biochar composite from rice husk and rice bran exhibited BPA degradation efficiency of RB-MBC (94.25%) (Chu et al. 2021). Also, magnetic biochar synthesized from Magnetic Biochar from *Zea mays* husk had an adsorption capacity of 23.60 mg/g and 22.53 mg/g for Ni(II) and Cu(II) (Isaac and Siddiqui 2022). (Isaac et al. 2023) applied magnetic *Juglans Regia* shell biochar as an adsorbent for the removal of Cu^{2+} and Ni^{2+} . The result of their study showed maximum adsorption capacities of 16.83 mg/g and 18.11 mg/g respectively under optimum conditions using aqueous solutions. Hence, these results indicate that the performance of CSMB adsorbent offers an excellent performance as compared with other magnetic biochar adsorbents. Furthermore, the reusability of CSMB was validated over five adsorption-desorption cycles, with only a slight decline in adsorption capacity from 43.5 mg/g to approximately 41 mg/g, confirming its sustainability and cost-effectiveness as an adsorbent for water treatment applications. The results of this study demonstrate that CSMB is a highly efficient adsorbent for BPS removal, with superior adsorption capacity and reusability compared to other magnetic biochar adsorbents. Its eco-friendly nature, derived from renewable coconut shell waste, further enhances its appeal as a sustainable solution for addressing water pollution challenges.

Conclusion

This study presents the first investigation into the synthesis and application of magnetic biochar derived from coconut shell waste, a by-product of the palm oil mill industry, for the removal of bisphenol S (BPS) from aqueous solutions. The coconut shell magnetic biochar (CSMB) was synthesized through pyrolysis and co-precipitation techniques. Comprehensive characterization using FTIR, FESEM, XRD, BET, EDX, and VSM confirmed the successful incorporation of iron, forming CSMB. The CSMB exhibited a high surface area of $373 \text{ m}^2/\text{g}$ and demonstrated superior adsorption capacity for BPS, achieving 43.5 mg/g compared to 26.7 mg/g for conventional coconut shell biochar (CSB). The adsorption process

parameters were evaluated through batch experiments. The optimal adsorption conditions were identified at pH 6.0 with a maximum capacity of 52.3 mg/g. Kinetic studies demonstrated that the pseudo-second-order model best described the adsorption kinetics of CSMB. The adsorption process was found to be highly dependent on the solution pH, with maximum removal capacities observed at pH 6.0.

The reusability of the CSMB sorbent was assessed through five consecutive adsorption-desorption cycles at ambient temperature. The CSMB showed remarkable reusability, maintaining high adsorption efficiency over five cycles with only a slight decrease in capacity from 43.5 mg/g to approximately 41 mg/g. This indicates that CSMB is a sustainable and effective adsorbent for water treatment applications compared to other sorbents. The cost estimation analysis revealed that the total cost of producing CSMB was approximately 158.37 MYR (around \$36.43) for 10 kg, translating to about \$3.64 per kg. This cost is competitive when compared to other biochar adsorbents, which range from \$0.56 to \$5.49 per kg. These findings demonstrate that coconut shell-derived biochars, both with and without magnetic properties, are inexpensive and efficient sorbents with potential applications in the remediation of organic pollutants, such as pharmaceutical wastewater. A promising approach for managing and efficiently utilizing this waste stream is the conversion of abundant bio-based industrial waste by pyrolysis into value-added biochar.

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Disclosure statement

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