

Article

Pore-Engineered Magnetic Biochar: Optimizing Pyrolysis and Fe₃O₄ Loading for Targeted Chlorinated Aliphatic Hydrocarbon (CAH) Adsorption

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Abstract

Chlorinated aliphatic hydrocarbons (CAHs) are some of the most widely distributed organic pollutants in underground environments and have high biological toxicity. This research aims to prepare an effective adsorbent comprising biochar and magnetite (MBC) to remove CAH pollution from soil. Optimization of the preparation and adsorption performance of MBC was investigated. The results of the adsorption experiment, combined with scanning electron microscopy (SEM) observations, show that the best raw material and pyrolysis temperature were coconut shell and 500 °C respectively. The Fourier transform infrared (FTIR) and X-ray diffraction (XRD) pattern characterizations, as well as the adsorption results, demonstrated the successful synthesis and enhancement effect of MBC for CAHs. The adsorption of CAHs on Fe₃O₄-loaded biochar was improved by 34.40–222.25% during pyrolysis at 500–900 °C. Additionally, MBC with a 10% Fe₃O₄ content had the best effect on three types of CAHs at low concentrations. A comparative pore analysis of MBC with different doses of Fe₃O₄ was carried out to reveal the relationship between the pore characteristics and adsorption properties. Furthermore, competitive adsorption experiments demonstrated that 4 wt% MBC addition significantly reduced the soil-bound TCE by 48.6%. Overall, these results indicated that MBC was an effective adsorbent for CAH removal from the polluted underground environment.

Keywords: magnetic biochar; adsorbent; chlorinated aliphatic hydrocarbons (CAHs); soil remediation; porous material



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1. Introduction

Chlorinated aliphatic hydrocarbons (CAHs) are a kind of ubiquitous pollutant that are often classified as dense non-aqueous phase liquids (DNAPLs). Due to the improper use and disposal of some industrial activities, they often appear in groundwater [1]. These compounds are pervasive environmental contaminants, with approximately 71% of urban groundwater in China contaminated by at least one CAHs species [2]. Their carcinogenic, teratogenic, and mutagenic properties (“three-induced effects”) pose severe risks to ecosystems and human health [3]. Regulatory frameworks, such as the U.S. ATSDR priority list and China’s GB36600-2018 standard [4], mandate stringent controls on CAHs, underscoring the urgency for effective remediation technologies to mitigate their environmental footprint [5].

Physical, chemical, and biological methods have been studied and attempted for the remediation of chlorinated-hydrocarbon-polluted sites. Strategies such as enhanced reduction using conductive materials, microbial and iron-based material synergistic approaches, and activated carbon adsorption are employed to address contamination by typical CAHs, including trichloroethylene, trichloroform, and chlorobenzene [6–8]. CAH pollutants in the underground environment are usually dispersed. Enriching them by adsorption first and then carrying out the following treatment is an effective treatment method [9]. Physical adsorption is the dominant adsorption of chlorinated organics in aquifers; therefore, it is necessary to develop effective adsorption materials and study their surface adsorption mechanism [10].

Biochar (BC) is an environmentally functional material possessing dual advantages of practical value and ecological benefits. It not only effectively removes target pollutants but also serves as an efficient carbon sink for engineered sequestration, offering multifaceted advantages. Biochar exhibits moderate reducibility, exceptional adsorption capacity, and electron transfer capability. These properties give it significant potential for removing chlorinated organic compounds, such as trichloroethylene (TCE) [11,12] and pentachlorophenol (PCP) [13]. Consequently, it has been extensively investigated for soil and groundwater remediation.

In recent years, iron–carbon composites (including nanoscale zero-valent iron (nZVI), iron oxides, iron hydroxides, and their composites) and pollutants have been widely researched for soil pollution remediation [14]. Biochar and magnetite have been demonstrated to facilitate the biotic and abiotic transformation of 1,2-dichloroethane, 2,4,6-trichlorophenol, and chlorobenzene [9,15–17]. As exogenous additives, these composites are increasingly being studied to enhance pollutant removal due to their good biocompatibility, high porosity, and strong adsorption capacity [18]. Among the diverse iron–carbon composites, biochar magnetite (MBC) has been widely studied for its excellent adsorption, reducibility, and electron transfer performance [19]. MBC can remove heavy metals (e.g., Pb^{2+} , Cr^{3+} , Cr^{6+} , Hg^{2+}) [20] and organic pollutants such as phenolic compounds (e.g., bisphenol A) [21], antibiotics (e.g., tetracycline) [22], and organic dyes (e.g., 2,4-difluoroaniline) [23] through electrostatic adsorption, ion exchange, redox reactions, and surface complexation. Magnetite and Fe (II) on the iron minerals surface can also play a reducing role in dechlorination of CAHs and elimination of pollutants such as carbon tetrachloride [24,25], dichloroethylene [26] and 1,2,3-trichloropropane [27]. For instance, studies demonstrate that their excellent electrochemical properties and adsorption capabilities promote the degradation of chlorinated organics, such as trichloroethylene (TCE) and atrazine (a chlorinated pesticide) [19,28]. Therefore, MBC can also remove chlorinated organics via adsorption, catalysis, and reduction from contaminated environment.

The application of MBC represents an effective remediation strategy for addressing CAH contamination in soil and groundwater. It utilizes the adsorptive property of the carbon matrix to preconcentrate pollutants, thereby enhancing subsequent chemical conversions and potentially supporting microbial detoxification. However, systematic research focusing specifically on the adsorption behavior of CAHs by MBC, especially under competitive conditions and in relation to material design, remains limited.

This study rationalized MBC composite design to enhance CAH removal. Pyrolysis and coprecipitation were applied to prepare biochar (BC) and MBC, respectively. Different feedstocks (coconut shell, peanut shell, and corn stover), pyrolysis temperatures (500–900 °C), and Fe_3O_4 ratios (10–100%) were investigated. Competitive adsorption experiments were used to investigate MBC's competitive adsorption capacity and remediation potential in CAH-contaminated soil. The results provide a rich reference for the adsorption of typical chlorinated hydrocarbon pollutants, and provide an economical and effective high-quality MBC composite material for the absorption of CAHs in underground environments.

2. Materials and Methods

2.1. Preparation of BC and $\text{Fe}_3\text{O}_4\text{@BC}$

Biochar (BC) was prepared from agricultural biomass wastes, including corn stalks, coconut shells, and peanut shells. The above-mentioned raw materials were first washed by deionized water under an ultrasonic treatment. Afterward, the cleaned material was dried at 105 °C, then pyrolyzed in a tubular furnace. The temperature was raised at a rate of 10 °C/min under a N_2 flow of 120 mL/min and the system was held at the target temperature for 2 h [29]. The obtained biochar derived from corn stalk, coconut shell, and peanut shell under different pyrolysis temperature were designated as YMBC, YKBC, and HSBC, respectively. Then, the obtained biochar was ground and sieved to a particle size of 100–200 mesh (75–150 μm) for further characterization and MBC preparation. In addition, biochar produced from coconut shells at 500 °C (YK500), 750 °C (YK750), and 900 °C (YK900) were prepared for comparison.

MBC was synthesized by the co-precipitation method. Briefly, 1.0 g of the prepared biochar was dispersed in 50 mL of oxygen-free deionized water under continuous stirring and heated to 80 °C. Subsequently, FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$ were added into the mixture at a molar ratio of 1:2 ($\text{Fe}^{2+}/\text{Fe}^{3+}$). The mixture was continuously stirred for 30 min to achieve complete impregnation of the iron ion into the biochar matrix. Then, ammonia solution was added dropwise to adjust the pH to 10–11, followed by 1 h of stirring. After aging the cooled mixture (25 °C) for 24 h, the precipitate was collected by filtration. Sequential washing with deionized water and anhydrous ethanol was performed until a neutral pH was achieved, followed by vacuum drying at 50 °C to yield MBC [30,31]. Specifically, MBC prepared from YK500, YK700, and YK900 with 10% Fe_3O_4 loading were labeled as YK500M, YK750M, and YK900M, respectively. Additionally, YK500 prepared with 10, 50, and 100 wt% Fe_3O_4 loading were designated as 10%MBC, 50%MBC, and 100%MBC, respectively.

2.2. Characterization of BC and $\text{Fe}_3\text{O}_4\text{@BC}$

Surface morphology and elemental composition of the samples were analyzed using scanning electron microscopy (SEM, Thermo Scientific Apreo 2S, Waltham, MA, USA) coupled with energy-dispersive X-ray spectroscopy (EDS, Bruker XFlash6 | 60, Billerica, MA, USA) [32]. Samples were sputter-coated with a 5 nm gold–palladium alloy prior to imaging at a 15 kV accelerating voltage. The crystal structure of BC and $\text{Fe}_3\text{O}_4\text{@BC}$ was characterized by the powder X-ray diffraction (XRD) pattern using a D8 advance diffractometer (Rigaku Ultima IV, Tokyo, Japan) with a Cu K α radiation source [33]. FTIR spectra were recorded on a Nicolet iS20 spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) [34] over 400–4000 cm^{-1} . The BET surface area and porosity were characterized using an ASAP 2460 analyzer (Micromeritics, Norcross, GA, USA) via N_2 adsorption–desorption isotherms at 77 K [35].

2.3. Adsorption Performance of BC and $\text{Fe}_3\text{O}_4\text{@BC}$

Dynamic gravimetric vapor sorption (DVS) analysis was conducted on a BSD-DVS instrument (Beishide Instrument Technology Co., Ltd., Beijing, China) to investigate the influence of the pyrolysis temperature (500, 750, 900 °C) and Fe/C ratio on the adsorption properties of all samples [36–38]. The gravimetric vapor sorption experiments were conducted using nitrogen as the purge gas. The measurements were performed at 25 °C, preceded by a degassing step at 200 °C for 180 min under an inert atmosphere. Trichloromethane (TCM), trichloroethylene (TCE), and chlorobenzene (CB) were calibrated based on their saturated vapor pressures at 25 °C, which are 26.32, 9.906, and 1.613 kPa, respectively. To determine the influence of the pyrolysis temperature on the adsorption capacities of the synthesized materials, adsorption capacities of YK500, YK750, and YK900, as well as their magnetic

composites YK500M, YK750M, and YK900M, were evaluated. To determine the impacts of different Fe₃O₄ loading levels on the adsorption capabilities, the TCM, TCE, and CB adsorption performances of YK500, 10%MBC, 50%MBC, and 100%MBC were evaluated.

2.4. BET Analysis and Calculation

The BET method employs N₂ as the adsorbate to characterize the surface area of samples by measuring the gas adsorption at varying pressures. According to the BET theoretical equations Equations (1) and (2), plotting $P/[V(P_0 - P)]$ against the relative pressure P/P_0 yields a straight line. The slope of this line equals $(C - 1)/CV_m$, while its intercept equals $1/CV_m$. The constant C and the monolayer adsorption capacity V_m can then be determined by simultaneously solving these slope and intercept relationships [39].

$$\frac{V}{V_m} = \frac{C \times P}{(P_0 - P)[1 + (C - 1)P/P_0]} \quad (1)$$

$$\frac{1}{V(\frac{P_0}{P} - 1)} = \frac{C - 1}{CV_m} \times \frac{P_0}{P} + \frac{1}{C} \quad (2)$$

where P_0 denotes the saturated vapor pressure of the adsorbate at the adsorption temperature (kPa), P represents the equilibrium gas pressure (kPa), V_m is the monolayer saturation adsorption capacity (mmol/g), V corresponds to the measured total adsorption quantity (mmol/g), and C is the characteristic constant of the BET equation.

The derived V_m value enables the calculation of the total number of molecules required to form a complete monolayer on the solid surface. With knowledge of the cross-sectional area occupied by a single adsorbate molecule, the samples' total and specific surface areas can be determined using Equation (3):

$$S = A_m \times N_A \times \frac{V_m}{22,400} \times 10^{-18} \quad (3)$$

where S is specific surface area (m²/g), A_m refers to the average cross-sectional area of a N₂ molecule (0.162 nm²), N_A is the Avogadro constant (6.02×10^{23}), and V_m is the monolayer saturation adsorption capacity (mmol/g). In this study, the pore size distribution of the samples was calculated based on the Barret–Joyner–Hallenda (BJH) model (mesoporous) and Horvath–Kawazoe model (micropore).

2.5. Characterization of Competitive Adsorption Between MBC and Soil

To study the adsorption capacity of MBC for chlorinated hydrocarbons in contaminated soil, competitive adsorption experiments were conducted. First, TCE-contaminated soil was prepared as follows: first, impurities in natural soil were removed through a 2 mm sieve. To ensure the uniformity of the TCE pollutants in the soil, a certain quality of natural soil was taken and its water content was adjusted to about 50% with deionized water; then, a certain quantity of TCE was dissolved in acetone solution and mixed in evenly with the natural soil to form a certain concentration of organic-TCE-contaminated soil. Then, 25 g of contaminated soil and 15 mL of deionized water were placed into a 40 mL sample bottle, and 0 g (CK), 0.5 g (2 wt%), or 1.0 g (4 wt%) of MBC was added. The bottles were prepared in duplicates to ensure reproducibility and allow for experimental errors to be estimated. After shaking at 120 rpm for 48 h at room temperature, the soil, MBC, and aqueous liquid were separated.

The concentration of chlorinated aliphatic hydrocarbons (CAHs) was determined using gas chromatography–mass spectrometry (GC–MS; Agilent 7890B/5977B equipped with an Atomx XYZ system, Agilent, Santa Clara, CA, USA) in accordance with the Chinese standard method HJ 643-2013 [40]. The headspace conditions were set as follows:

incubation at 80 °C with shaking for 35 min. The GC oven temperature program was initiated at 40 °C (held for 2 min), increased to 150 °C at 15 °C/min (held for 5 min), and then raised to 290 °C at 3 °C/min (held for 10 min). The MS operating parameters included an ion source temperature of 230 °C, a quadrupole temperature of 150 °C, and an injector temperature of 300 °C.

3. Results

3.1. Optimization of Biochar Sources and Pyrolysis Temperatures for Enhanced TCM Adsorption

The adsorption performances of biochars derived from different biomass sources (coconut shell, peanut shell, and corn stover) and pyrolyzed at varying temperatures (500, 750, and 900 °C) were evaluated using TCM as the target pollutant. As illustrated in Figure 1a, YKBC demonstrated the highest adsorption capacity, followed by HSBC and YMBC. Under the conditions of $P/P_0 = 0.1$ and 0.9, the adsorption capacities of YKBC were 2.27 and 1.24 times that of HSBC and 2.66 and 1.11 times that of YMBC, respectively. The adsorption capacity values of HSBC, YMBC, and YKBC were 30.89, 34.48, and 38.15 mg/g (measured at $P/P_0 = 0.9$), respectively. The well-developed porous architecture of YKBC (Figure 1b) may be a plausible explanation for its enhanced adsorption performance relative to biochars derived from other biomass sources (HSBC and YMBC, as shown in Figure 1c,d).

Furthermore, the pyrolysis temperature's effect on the adsorption performance of biochar was investigated. The significantly enhanced adsorption efficiency of YKBC pyrolyzed at 500 °C compared with those processed at 750 and 900 °C is shown in Figure 1e. Under the conditions of $P/P_0 = 0.1$ and 0.9, the adsorption capacities of 500YKBC were 7.82 and 5.08 times that of 750YKBC and 3.00 and 3.61 times that of 900YKBC, respectively. The decreased adsorptions of YKBC750 and YKBC900 may be attributed to pore collapse and a decrease in surface functional groups under elevated thermal conditions. As shown in Figure 1g,h, high pyrolysis temperatures (750–900 °C) induced structural collapse of the biochar micropores/mesopores through carbonization and thermal stress [41], reducing the surface area and adsorption capacity, whereas lower temperatures (500 °C) preserve hierarchical pore structures essential for TCM adsorption. Additionally, high-temperature treatments may deactivate oxygen-containing functional groups or alter the surface chemistry [42], further weakening interactions between biochar and TCM molecules. These findings emphasize the importance of optimizing the pyrolysis biomass sources and pyrolysis temperature for the effective adsorption of pollutants.

3.2. Validation of Fe_3O_4 Synthesis and Composite Characterization

Based on coconut shell biochar pyrolyzed at 500 °C (500YKBC), Fe_3O_4 -loaded biochar ($Fe_3O_4@BC$) was prepared using the coprecipitation method. The feasibility of $Fe_3O_4@BC$ was confirmed through comprehensive material characterization (Figure 2). Firstly, $Fe_3O_4@BC$ exhibited strong magnetic responsiveness via external magnetic fields (Figure 2a). The XRD analysis (Figure 2b) identified distinct peaks at $2\theta = 30.1^\circ$, 35.5° , 43.1° , 57.0° , and 62.6° , corresponding to the (2 2 0), (3 1 1), (4 0 0), (5 1 1), and (4 4 0) planes of the pure cubic spinel crystal structure of Fe_3O_4 with cell constant $a = 8.396 \text{ \AA}$ (JCPDS No. 19-0629), confirming successful crystallization. No impurity phases were detected, indicating the synthesized Fe_3O_4 's high purity. The SEM images and EDS elemental mapping (Figure 2c) revealed that synthetic nanoparticles containing Fe and O were uniformly dispersed on the biochar surface without significant aggregation. Combined with the above characterization, Fe_3O_4 was proved to be successfully compounded on the surface of BC and uniformly distributed.

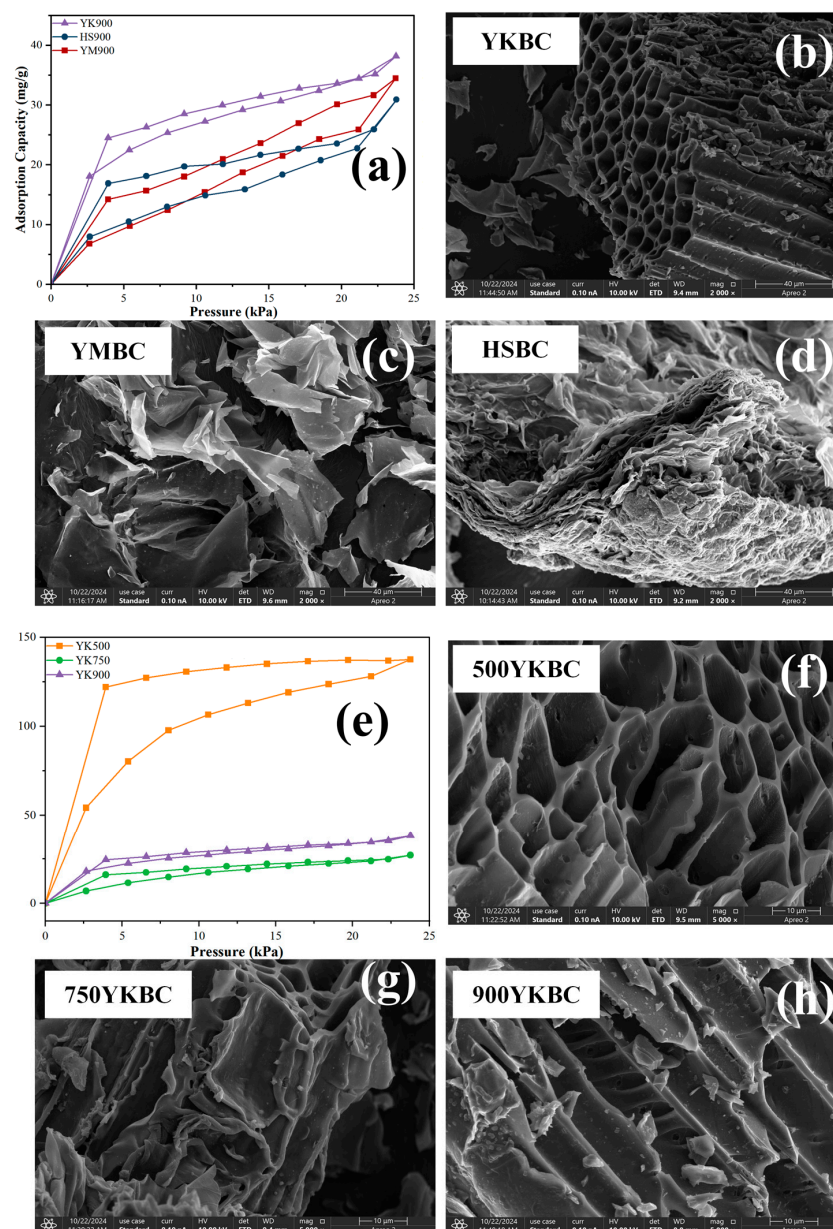


Figure 1. Adsorption of TCM on biochar prepared from different biomass sources and pyrolysis temperatures. (a–d) Adsorption curves and corresponding SEM images of biochars derived from different biomass feedstocks pyrolyzed at 900 °C; (e–h) adsorption curves and corresponding SEM images of coconut-shell-derived biochars prepared at different pyrolysis temperatures.

3.3. Enhanced TCM Adsorption Using Fe_3O_4 Loading and Mechanistic Insights

The impact of the Fe_3O_4 loading and pyrolysis temperature on the TCM adsorption was systematically investigated using YKBC pyrolyzed at 500, 750, and 900 °C (YK500, YK750, and YK900) as the base material. As shown in Figure 3a–c, the adsorption capacities of YK500M, YK750M, and YK900M reached 184.90, 101.98, and 122.96 mg/g, respectively, representing substantial increases compared with the non- Fe_3O_4 -loaded biochar samples YK500, YK750, and YK900, which exhibited capacities of only 137.58, 27.07, and 38.16 mg/g, respectively. Fe_3O_4 @BC (10% Fe_3O_4 by mass, YK500M, YK750M, and YK900M) exhibited 34.40, 276.68, and 222.25% higher adsorption capacities compared with the unmodified YKBC (YK500, YK750, and YK900, respectively). Nano- Fe_3O_4 itself had a good adsorption capacity [43], and the Fe_3O_4 particle deposition on the biochar made the surface rough and

increased the specific surface area (Figure 2c), which improved the adsorption performance of the material.

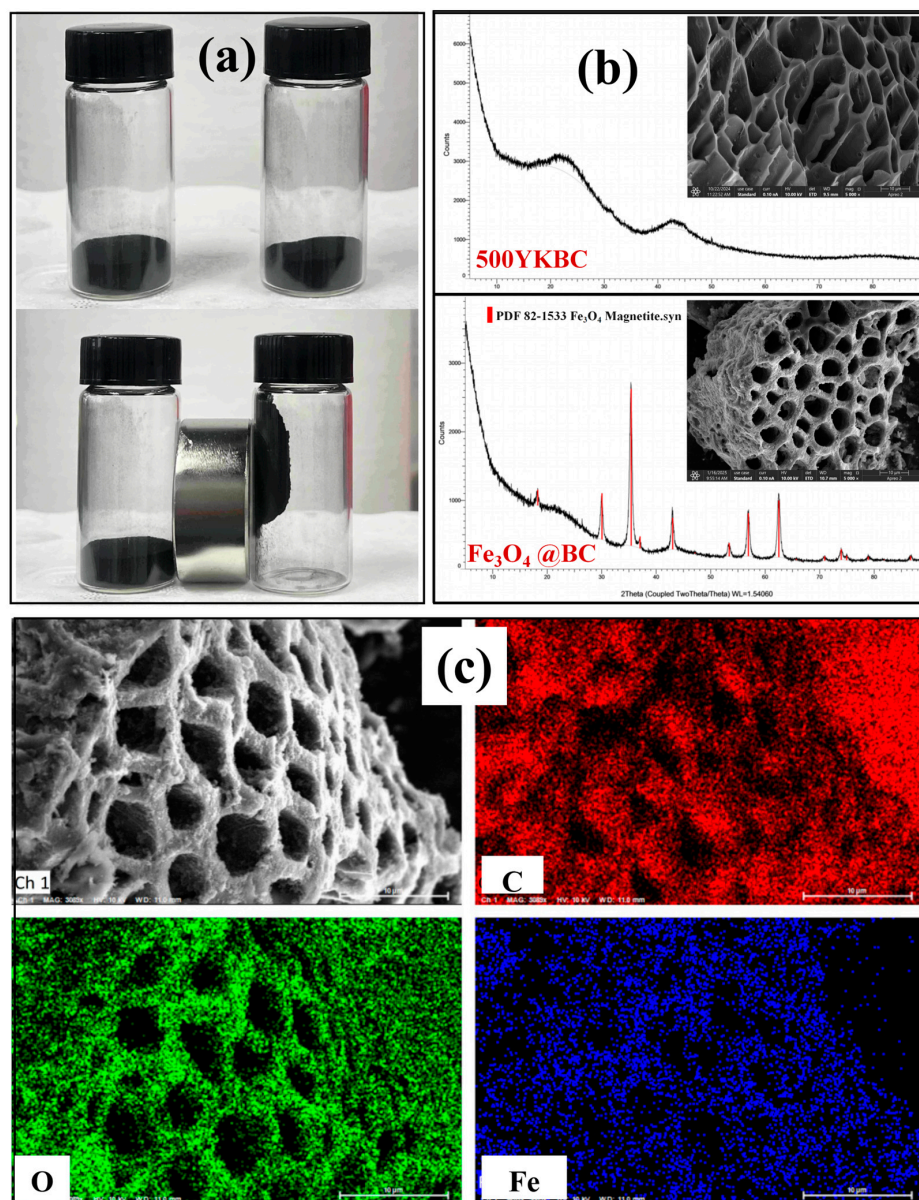


Figure 2. Magnetic observation (a), XRD (b), and SEM with EDS (c) characterizations of Fe₃O₄@BC and BC.

Moreover, the excellent adsorption capacities of YK500 and YK500M demonstrated that 500 °C was a more suitable pyrolysis temperature for the biochar adsorbing TCM compared with a higher temperature. An increase in pyrolysis temperature is advantageous for enhancing the conductivity of biochar but is detrimental to the retention of functional groups [42]. The adsorption of organic matter on the surface of biochar is mainly due to functional groups rather than the influence of conductivity. Therefore, the biochar obtained from relatively low-temperature pyrolysis and its Fe₃O₄-modified products were more suitable for TCM adsorption in this study.

Additionally, the enhancement could be attributed to the incremental chemisorption facilitated by Fe₃O₄. FTIR was applied to characterize the change in functional groups between before and after the TCM adsorption of BC (YK500) and Fe₃O₄@BC (YK500M), which provided critical insights into the adsorption mechanism. First, the significant shift

in the -OH stretching vibration absorption peak ($3000\text{--}3500\text{ cm}^{-1}$ of BC) indicates that the hydroxyl groups on the surface of biochar form hydrogen bonds or coordinate with the Fe^{2+} or Fe^{3+} , which is also an important characteristic of Fe_3O_4 loading [44]. Additionally, Figure 3d shows absorption peaks at 1566 and 1381 cm^{-1} , which are located in the aromatic characteristic absorption region and related to the C=C stretching vibration of biochar [45]. The absorption peaks near 1074 and 876 cm^{-1} are mainly related to C-O and C-H. These peaks shifted due to the influence of loaded iron oxide and adsorbed TCM [46]. Moreover, for pristine YK500, no significant chemical shifts or new peaks were observed after TCM adsorption, suggesting that the adsorption primarily occurred via physical entrapment within micropores. In contrast, $\text{Fe}_3\text{O}_4\text{@BC}$ displayed a prominent absorption band at 732 cm^{-1} post-adsorption, corresponding to the C-Cl stretching vibration of TCM. The results indicate that the loading Fe_3O_4 introduced active surface sites capable of forming coordination complexes with TCM molecules. In general, Fe-O active sites can form Fe-O-Cl through oxygen bond coordination [47]. Although this was not measured in this study, this could still be a potential function. Consequently, the improvement in adsorption performance following the loading of Fe_3O_4 was influenced by both physical (pore filling, electrostatic adsorption) and potentially chemical (Fe-O-Cl complexation) factors.

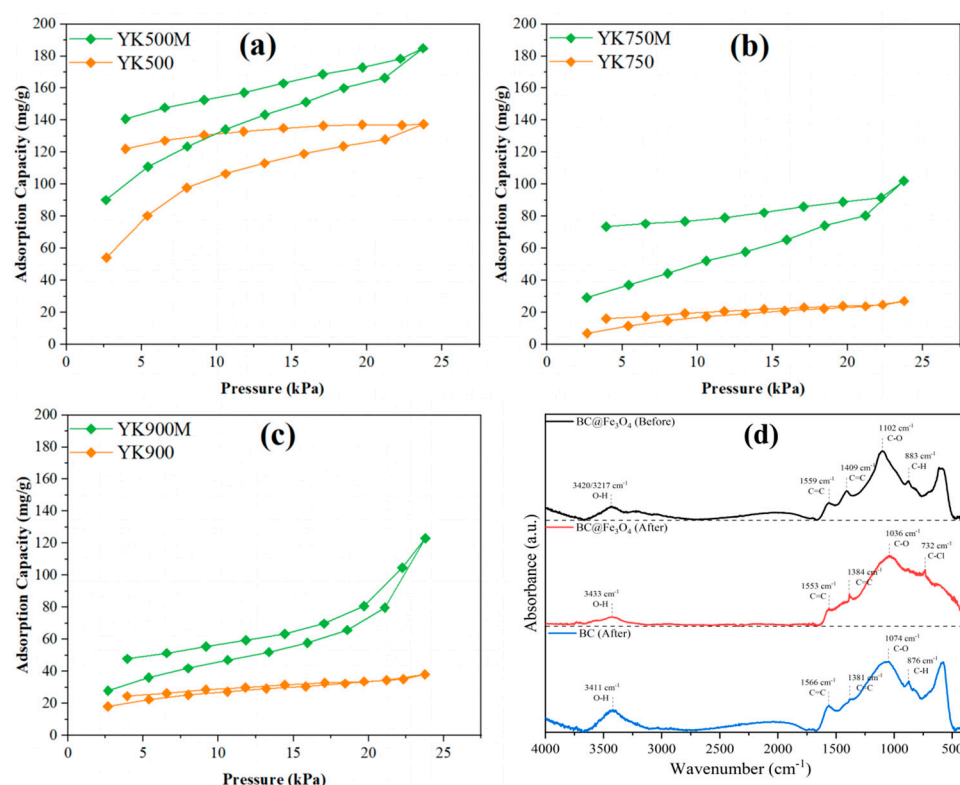


Figure 3. (a–c) The adsorption isotherms of TCM on BC (YK500, YK750, and YK900) and $\text{Fe}_3\text{O}_4\text{@BC}$ (YK500M, YK750M, and YK900M). (d) FTIR spectra of YK500 and YK500M after absorbing TCM.

3.4. Influence of Fe_3O_4 Loading Ratios on Adsorption Performance of Typical CAHs

The relationship between the Fe_3O_4 content (10, 50, and 100% by mass) and adsorption performance of typical chlorinated hydrocarbons (TCM, TCE, and CB) was evaluated (Figure 4). First the synthesized materials exhibited a significantly enhanced adsorption performance toward CAHs compared with previously reported carbon-based adsorbents. The saturated adsorption capacities (measured at $P/P_0 = 0.95$) of CB on 10%MBC, 50%MBC, and 100%MBC were 147.78, 162.17, and 198.72 mg/g, respectively—significantly higher than 87.06 mg/g of 50YKBC. These values also exceed the range of 15.1–123.4 mg/g reported for functionalized carbon materials [8]. Moreover, the adsorption capacities for

TCE all exceeded 100 mg/g, considerably higher than the value of 55 mg/g documented in [11]. This fully demonstrates that modification with ferric oxide is an effective method for improving the adsorption of CAHs on biochar.

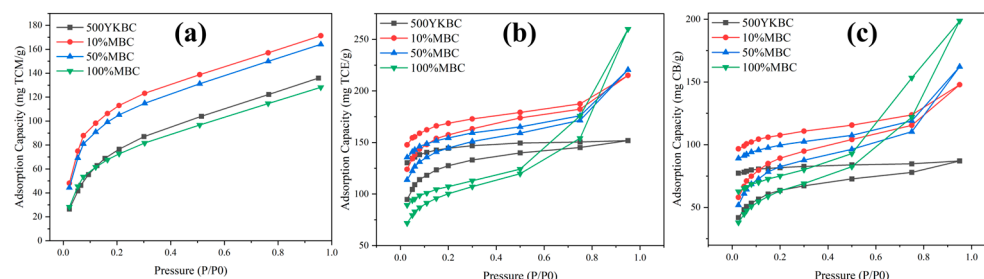


Figure 4. The adsorption isotherms of TCM (a), TCE (b), and CB (c) on 500YKBC and Fe₃O₄@BC (10%MBC, 50%MBC, and 100%MBC).

Additionally, differences in the adsorption performance were observed between the materials with varying Fe₃O₄ loadings toward different CAHs. 10%MBC showed the best adsorption capacity in the adsorption of three types of chlorinated hydrocarbons (TCM, TCE, and CB), especially in the adsorption determination of TCM (Figure 4a). Different contents of Fe₃O₄@BC exhibited a 10%MBC > 50%MBC > 500YKBC > 100%MBC ranking from low concentration to close to the saturation concentration of TCM. For relatively large molecules, such as TCE and CB, at low concentrations, the adsorption capacity of different materials still showed a 10%MBC > 50%MBC > 500YKBC > 100%MBC ranking. However, at higher concentrations (Figure 4b,c), 100%MBC exhibited the most outstanding adsorption. 50%MBC also showed a reinforced adsorption capacity and exceeded that of 10%MBC at P/P₀ = 0.95.

In general, the 10%MBC exhibited the highest adsorption capacity for three chlorinated hydrocarbons (CHCs)—TCM, TCE, and CB—at low concentrations. Regarding the small molecule TCM, 100%MBC even performed worse than 500YKBC without Fe₃O₄, while it demonstrated greater adsorption than 10%MBC and 50%MBC for larger molecules, such as TCE and CB, at high concentrations. Meanwhile, 100%MBC exhibited the greatest adsorption for large molecules, such as TCE and CB, at high concentrations.

3.5. Comparative Pore Analysis of the Synthetic Materials

The BET surface area, pore size, and pore volume distribution of the composites were analyzed using a BET analyzer. It is generally believed that the larger the specific surface area of an adsorbent, the stronger its adsorption capacity [48]. However, a nonlinear phenomenon was observed in this study. This nonlinear trend can be explained by the following factors: A small amount Fe₃O₄ nanoparticles provided abundant active sites and a high surface area without blocking biochar pores at the lower addition of 10%, maximizing the absorption contributions on the surface of biochar [48]. Excessive Fe₃O₄ (>50%) led to nanoparticle aggregation, which hindered micropores and reduced the micropore surface area, as well as the general (BET) surface area of biochar (Figure 5). However, the aggregation of Fe₃O₄ nanoparticle increased the mesopore surface area and mesopore pore volume, which also provided multilayer adsorption potentiality. The large molecules, such as TCE and CB, preferred to be absorbed by pores larger than mesopores.

Certainly, this correlation arises from molecular size effects, differences in diffusion kinetics, and the surface chemical properties of the various CHAs molecules, rather than from molecular size alone. Here, molecular size is referred to solely to distinguish between the three CAH species used in the experiments. Notably, 100%MBC exhibited the greatest adsorption compared with 10%MBC and 50%MBC for TCE and CB at high concentrations.

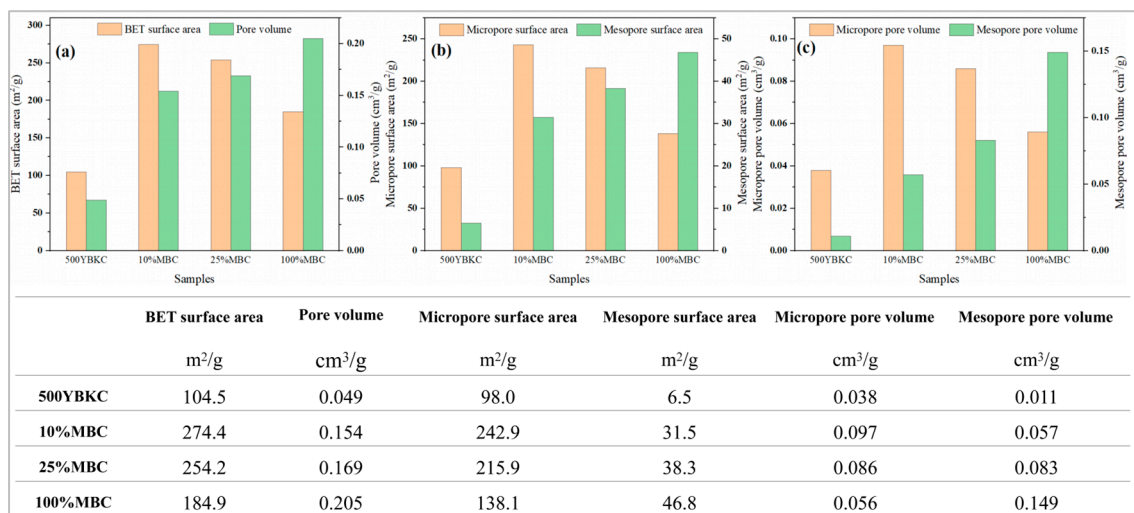


Figure 5. Comparative pore analysis of 500YBKC and $\text{Fe}_3\text{O}_4\text{@BC}$ (10%MBC, 50%MBC, 100%MBC): micro/mesoporous surface area (a,b) and pore volume (c).

3.6. Competitive Adsorption Between MBC and Soil

As shown in Figure 6, in the control group (CK) without MBC, the soil retained 11.13 $\mu\text{g/g}$ of TCE, while the liquid-phase TCE reached 51.08 $\mu\text{g/L}$, establishing baseline partitioning. Upon adding 2 wt% MBC, the soil TCE decreased to 9.64 $\mu\text{g/g}$, with the liquid phase at 48.98 $\mu\text{g/L}$ and MBC adsorbing 115.27 $\mu\text{g/g}$ of TCE. More strikingly, at 4 wt% MBC loading, the soil TCE further dropped to 5.72 $\mu\text{g/g}$, a 48.6% reduction compared with CK. Meanwhile, the MBC adsorption surged to 138.70 $\mu\text{g/g}$ and the aqueous TCE declined markedly to 27.77 $\mu\text{g/L}$.

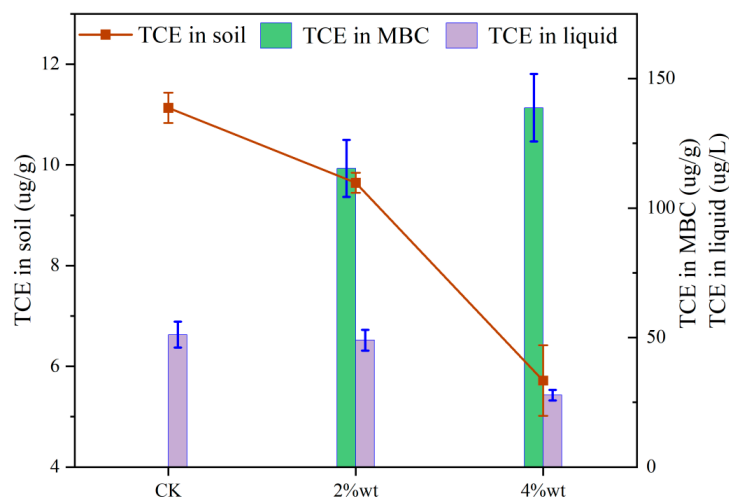


Figure 6. Dose–response of MBC on TCE sequestration from contaminated soil.

4. Discussion

Adsorption experiments, combined with scanning electron microscopy (SEM), revealed that coconut-shell-derived biochar pyrolyzed at 500 °C exhibited the optimal performance. The successful synthesis of MBC and its enhanced adsorption capacity for CAHs were further confirmed using FTIR, XRD, and the corresponding adsorption results.

The adsorption process is generally influenced by the surface area of the material, pore structure, chemical functional groups, and the interactions between the adsorbate and the adsorbent [49]. The pore properties of MBC with different loading rates of iron oxide also

vary, which, in turn, affect the adsorption performance of MBC on CAHs with different concentrations and molecular weights.

The results of the pore properties combined with the adsorption demonstrated that the adsorption of low-molecular-weight chlorinated hydrocarbons (such as TCM) is primarily governed by the general specific surface area and micropore structure, whereas the adsorption of high-concentration, near-saturation, large-molecular-weight chlorinated hydrocarbons (such as TCE and CB) is predominantly influenced by mesoporous structures. According to the above results, the Fe_3O_4 loading ratios in MBC should be optimized based on the characteristics of the target pollutant (such as molecular weight and concentration).

Although the experimental results confirm that the presence of Fe_3O_4 enhances the CAH adsorption performance of biochar, the underlying chemical and physical mechanisms cannot be fully elucidated using FTIR analysis alone. The relationship between the textural properties (e.g., porosity, pore size distribution) and the adsorption behavior warrants more systematic and in-depth investigation. Further experimental results demonstrated that MBC actively competes for TCE adsorption in soil matrices, effectively immobilizing CAHs, thereby positioning it as a highly effective adsorbent for remediating CAH-contaminated soil systems. The material developed in this study is designed not only to efficiently adsorb CAHs but also to enable subsequent degradation of the concentrated pollutants through iron-mediated reduction or microbial processes. Moreover, the electron shuttle effect of Fe_3O_4 mediates microbial electron transfer and biogeochemical reactions in the underground environment and has the potential to promote pollutant degradation in a synergistic manner. Therefore, future research will focus particularly on elucidating the electron transfer mechanisms of Fe_3O_4 and the $\text{Fe(II)}/\text{Fe(III)}$ redox processes involved in the degradation pathway.

Preliminary experiments have confirmed the adsorption effect of magnetic biochar (MBC) on typical chlorinated hydrocarbons. In practical applications, site applicability requires strict verification of the compatibility of materials with aquifer conditions (e.g., soil permeability, groundwater velocity, pollutant plume range/concentration), and evaluation of the MBC migration performance. Future research on MBC for CAH remediation should extend beyond the sorption capacity to elucidate its role in mediating microbial degradation and facilitating electrochemical reduction processes.

5. Conclusions

Biochar derived from coconut shell at 500 °C exhibited high structural integrity and adsorption affinity for various CAHs. Fe_3O_4 loading significantly enhanced the CAH removal via synergistic effects, with 10 wt% Fe_3O_4 being optimal for small or low-concentration CAHs (e.g., TCM), and 100 wt% Fe_3O_4 being the most effective for high-concentration macromolecular CAHs (e.g., TCE, CB). MBC also demonstrated potential for TCE release in contaminated soil, confirming its promise as a versatile remediant for CAH pollution.

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