Research article

Simultaneous adsorption of fulvic acid and organic contaminants by KOH activated mesoporous biochar with large surface area

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ABSTRACT

Returning carbon materials from biomass to soil is a potential technology to retard organic contaminants or dissolved organic matter (DOM) in soil by adsorption, as well as to store carbon in soil for carbon sequestration. However, DOM was widely reported to inhibit adsorption of organic contaminants on carbon materials by competition and by enhancing contaminants' solubility. In this study, a KOH activated carbon material (KAC), pyrolyzed from bamboo chips, with high surface area (3108 m^2/g), micropores volumes (0.964 cm^3/g), mesopores volumes (1.284 cm^3/g), was observed that it can adsorb fulvic acid (FA) and organic contaminants (e.g., nitrobenzene, phenols, and anilines) simultaneously with weak competition and high adsorption capacity. With 50 mg TOC/L FA, for example, the average competition suppressing rate ($\Delta K_f/K_{f\text{-}m}$) of organic contaminants on KAC was lower than 5%, the adsorption for organic contaminants and FA were higher than 1100 mg/g and 90 mg TOC/g, respectively. The weak competition on KAC could be attributed to the low micropore blockage ($<$35%) and the weak adsorption sites competition on mesopores of KAC, as well as the minimal solubility enhancement of organic contaminants by FA because most FA is adsorbed on KAC but is not dissolved in the solution. In addition, adsorption of organic contaminants with high hydrogen-bonding donor ability (α_m) and adsorption affinity was less suppressed by FA because of the heterogeneous nature of hydrophilic sites on KAC's surface. Therefore, KAC could be a potential carbon material to be produced to implement to soil for carbon storage and simultaneous retarding organic contaminants and DOM.

1. Introduction

Converting biomass residues (e.g., crop straw, wood, manure, and bamboo chips) into stable carbon materials like biochar and subsequently returning them to soil is a prospective solution for carbon sequestration [1–4]. Meanwhile, biochar with large surface area and developed pores has been recommended as soil amendment materials for retarding organic contaminants as well as dissolved organic matter (DOM) by adsorption [5–7].

Many studies have shown that DOM inhibited the adsorption of organic contaminants on carbon materials by competition for limited adsorption sites or micropore blockage [8–10], as well as enhancing the solubility of some organic solutes [11–14]. Therefore, carbon materials, with more adsorption sites and wider pore size, would be helpful to resist the competition of organic contaminants by DOM. For example, some researchers have found that by expanding the pore size of carbon materials and improving the proportion of mesopores, adsorption competition of organic contaminants by DOM could be suppressed [8,15,16]. Moreover, it has been reported that increasing the volume of mesopores was conducive to improving the adsorption of macromolecules like DOM [17,18] and thus decreasing the DOM concentration in soil water, which would be helpful to avoid the solubility enhancement of organic contaminants by DOM in soil water. Therefore, it can be inferred that carbon materials with large surface area and wide pore distribution combining more mesopores could provide abundant adsorption sites for both organic contaminants and DOM, and thus effectively reducing adsorption competition to achieve higher simultaneous adsorption capacity.

With further activation of biochar through physical and chemical methods, the product could have increased surface area and more developed pore structure [19–21]. For example, with carbon dioxide or steam as an activating agent, the activated products could have specific surface area <1500 m^2/g and pore volume <0.9 cm^3/g are normally obtained [22,23]. Compared with physical activation, chemical activation with activating agents such as KOH, $ZnCl_2$ and H_3PO_4 could give rise to porous carbon materials with higher surface area and large pore volume [24]. Among the various activating agents, carbon materials activated by KOH exhibit large surface area >3000 m^2/g and pore volume >1.8 cm^3/g [22,24–26], while for other activating agents, the surface areas are normally <2000 m^2/g and pore volumes <1.5 cm^3/g [22–24]. Meanwhile, KOH activated carbon materials were observed to exhibit higher adsorption for DOM than many other carbon materials [27] and enhanced adsorption performance of tetracycline antibiotics [28,29] and toxic metals [30]. Based on the analysis above, this KOH activated biochar could have the potential to mitigate the adsorption competition between organic contaminants and DOM, resulting in substantial simultaneous adsorption.

Therefore, in this work, adsorption of organic contaminants (i.e., nitrobenzene, phenols, and anilines) with fulvic acid (FA), the most soluble component of DOM, on a KOH activated biochar (KAC), pyrolyzed from bamboo chips, was investigated. This study aimed to verify the potential ability of KAC for retarding organic contaminants and FA simultaneously, and to reveal the simultaneous adsorption mechanisms. To our best knowledge, it was the first study to focus on mitigating the competition inhibition of organic contaminants by FA with KOH activated biochar, in order to achieve a high simultaneous adsorption capacity for both organic contaminants and FA. The findings will help to provide advanced biomass-based carbon materials for soil organic pollution remediation and DOM immobilization as well as carbon sequestration.

2. Materials and methods

2.1. Chemicals and reagents

KAC was prepared from bamboo chips with the method described in our previous research [27]. The Surface area calculated by multipoint Brunauer-Emmett- Teller (BET) method at p/p^0 of 0.05–0.3 [7] was 3108 m^2/g. Total pore volume (V_{tot}) measured at p/p^0 about 0.99 [31] was 2.248 cm^3/g. Micropore volume (V_{mic}) calculated by Dubinin-Raduskevich method was 0.964 cm^3/g, and mesopores volume (V_{mes}) was 1.284 cm^3/g calculated by V_{tot} - V_{mic} (Table S1). FA (+95%), a dark brown powder, was purchased from Shanghai JiangLai Biological Co. Nitrobenzene (+99%) was purchased from Acros Organics Co. 2-Nitroaniline (+99%), 2-chloroaniline (+98%) and 4-chlorophenol (+99%) were purchased from Aladdin Reagent Co. 4-Nitroaniline (+99.5%), 4-methylphenol (+98%) and 3-nitrophenol (+99%) were purchased from Shanghai Reagent Co. All these chemicals were used as received. Their physicochemical properties are listed in Table S1.

2.2. Batch adsorption experiments

Adsorption experiments in mono-component and binary-component systems were conducted at 25 ± 1 °C. FA solution was obtained by dissolving FA powder in deionized water. Other chemicals were dissolved in background solution containing 0.01 mol/L $CaCl_2$. The ratio between the mass of KAC and the solution volume in both mono-component and binary-component systems was predetermined through pre-experimentation to achieve a >20% removal of adsorbates. Solution pH was adjusted using 0.1 mol/L HCl and 0.1 mol/L NaOH to achieve an equilibrium pH of 5.5 ± 0.3. For kinetics adsorption experiments, 2.5 mg KAC was added in 8 ml vials containing 100 mg TOC/L of FA and 100 mg/L of organic contaminant, then, the vials were placed in a 150 rpm shaker and taken at various time intervals to determine the residual concentrations of FA and organic contaminant in solution. Kinetic data (Fig. S1) showed that adsorption of organic contaminants (i.e., nitrobenzene, 2-nitroaniline, 4-nitroaniline, 2-chloroaniline, 4-methylphenol, 4-chlorophenol and 3-nitrophenol) in mono-component and binary-component systems increased rapidly initially and then slowed to reach equilibrium about 48 h. As for FA, the adsorption gradually increased to reach equilibrium at 5 days with or without organic contaminants. Batch competitive adsorption experiments of organic contaminants by FA were conducted at a given concentration of FA, with the initial concentrations of organic contaminants ranging from 0.01 to 0.85 S_w (water solubility). The mixtures in vials were shaken at 150 rpm for 5 days to reach equilibrium. After equilibrium, the mixtures were separated by centrifugation at 3500 rpm for 30 min and followed by filtration through 0.45 mm membranes. Equilibrium concentrations of FA and organic contaminants were quantified using Liquid Chromatography (Shimadzu, LC-20A, Tokyo, Japan) equipped with a UV-detector at the wavelength of 254 nm for FA and the maximum absorption wavelength (λ_{max}) for organic contaminants listed in Table S1. Here the organic carbon concentrations of FA (mg TOC/L) were obtained by the conversion between organic carbon concentration measured with total organic carbon (TOC) analyzer and absorbance at 254 nm measured with UV–visible spectrophotometer [27]. Detailed detection information

of the mobile phase composition and the liquid chromatography diagram for organic contaminants and FA were given in Table S2 and Fig. S2, respectively. Experiment uncertainties were evaluated in vials without KAC, which showed that total uncertainty was less than 3% of the initial adsorbate concentrations. Therefore, the adsorbed amounts of organic contaminants and FA by KAC were calculated
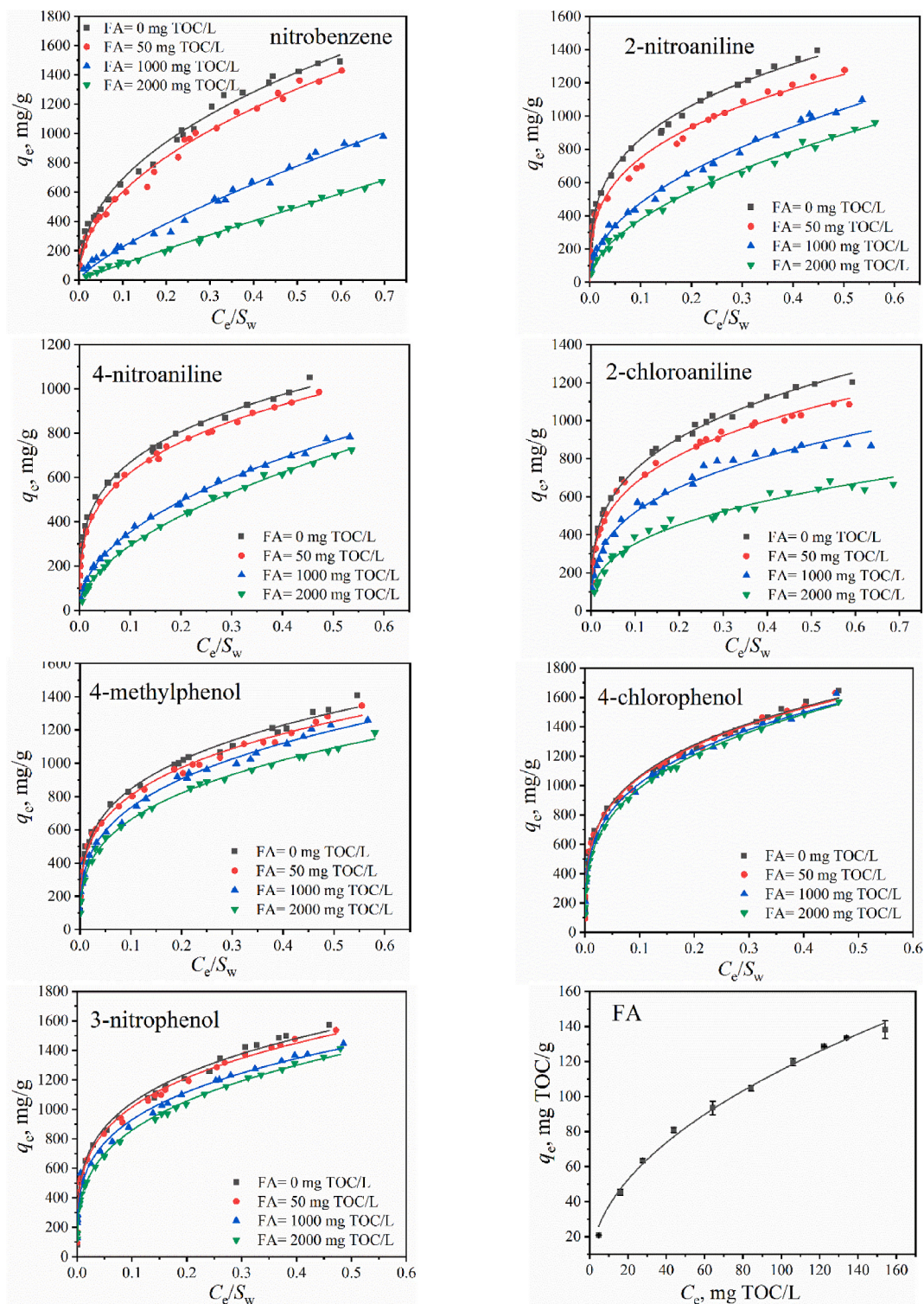

Fig. 1. Isotherms of nitrobenzene, 2-nitroaniline, 4-nitroaniline, 2-chloroaniline, 4-methylphenol, 4-chlorophenol, 3-nitrophenol and FA on KAC. Solid lines represent isotherms fitted by Freundlich model.

from the mass difference in initial and equilibrium solutions.

2.3. Models and data analysis

Isotherm models, Freundlich model in Eq. (1), widely used in the literatures [10,16–19,27], was employed to fit the adsorption of FA and organic contaminants. Polanyi theory-based Dubinin-Astakhov (DA) model in Eq. (2) [32], which has been successfully used in fitting isotherms of organic contaminants by KOH activated carbon and other adsorbents both in mono-component and binary-component systems [23,33–35], was also employed here to fit the isotherms of organic contaminants, but not FA. Because FA, as a heterogeneous mixture, has no specific water solubility value available.

$$q_e = K_f \times C_e^n \tag{1}$$

$$\log q_e = \log Q^0 - (\varepsilon/E)^b \tag{2}$$

$$Q^0 = K_f \times S_w^n \tag{3}$$

$$E = 5.71 \times n \tag{4}$$

where q_e (mg/g) is the equilibrium adsorbed amount of adsorbates on KAC, K_f [(mg/g)/(mg/L)^n] is the Freundlich affinity coefficient, and n is the Freundlich exponential coefficient. Q^0 (mg/g) is the saturated adsorption capacity of organic contaminants by KAC. The ε (kJ/mol) is the effective adsorption potential obtained by $\varepsilon = RT\ln(S_w/C_e)$. R (8.314×10^{-3} kJ/(mol·K)) is the universal gas constant; T (K) is the absolute temperature. S_w (mg/L) is the water solubility. C_e (mg/L) is the equilibrium concentration of organic contaminants in aqueous phase. E (kJ/mol) is the adsorption affinity representing the strength of interactions [32,33,35]. The b is a fitted parameter. Actually, Freundlich model is the special form of DA model at the parameter $b = 1$ [33,36]. The sorption capacity Q^0 can be calculated from the Freundlich model coefficient K_f and S_w using Eq. (3), and the sorption affinity E can be calculated from the exponential coefficient n of the Freundlich model using Eq. (4) [33,36]. SPSS 26.0 software was used to perform the statistical analysis. Origin 2018 was employed in the data graphing.

3. Results and discussion

3.1. Adsorption of organic contaminants by KAC with FA

Effect of the initial concentrations of FA in the range of 50–4000 mg TOC/L on the adsorption of organic contaminants at a given concentration in binary-component systems was investigated (Fig. S3). With increasing initial concentrations of FA, adsorption of selected organic contaminants decreased rapidly and then gradually slowed down when the concentrations of FA were higher than 2000 mg TOC/L. Thus, 2000 mg TOC/L was selected as the highest concentration to investigate the competition effects of FA for the adsorption of organic contaminants on KAC. Adsorption isotherms of selected organic contaminants and FA on KAC in mono-component and binary-component systems were displayed in Fig. 1. Relevant parameters obtained from Freundlich model were summarized in Table S3. Isotherm fitted with model equations is a key issue to interpret the experiment data and explore adsorption mechanisms. Freundlich model was widely used in the literatures to fit the adsorption of FA [17,18,27] and organic contaminants [10, 16,19]. According to Eq. (1), with various equilibrium concentrations C_e and corresponding adsorption capacity q_e of adsorbates in
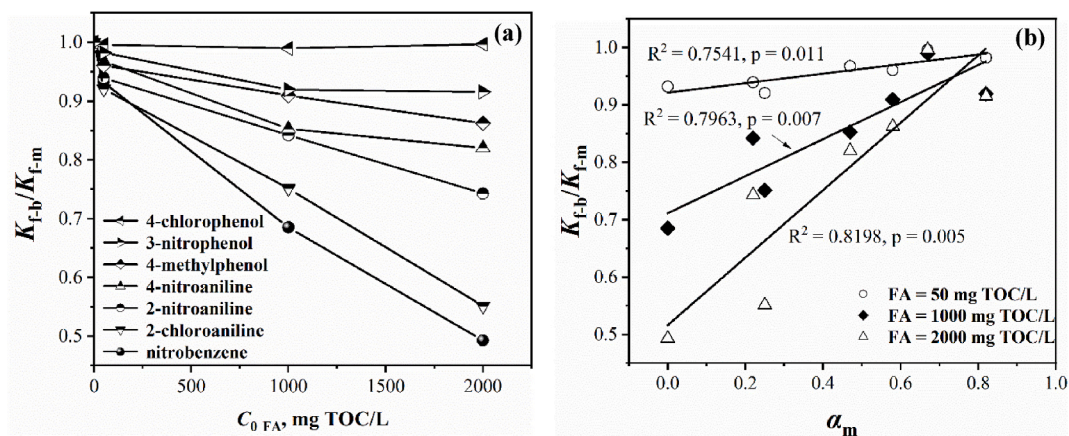

Fig. 2. Effects of FA on the competition inhibition degree parameter K_{f-b}/K_{f-m} of nitrobenzene, 2-nitroaniline, 4-nitroaniline, 2-chloroaniline, 4-methylphenol, 4-chlorophenol, 3-nitrophenol on KAC (a), and the correlations between K_{f-b}/K_{f-m} and hydrogen-bonding donor ability (α_m) of the organic contaminants (b).

aqueous phase, relevant parameters obtained from Freundlich model can be obtained (Table S3). With increasing concentrations of FA, adsorption for all organic contaminants decreased. However, the competition inhibition degrees of these organic contaminants by FA were various, indicated by the isotherms (Fig. 1) and the difference of the decreasing in Freundlich affinity coefficient K_f and exponential coefficient n (Fig. S4). The competition inhibition degree parameter K_{f-b}/K_{f-m}, the ratios of the affinity coefficient (K_f, $(mg/g)/(mg/L)^n$) of organic contaminants in binary-component systems (K_{f-b}) and in mono-component system (K_{f-m}) were calculated (Table S3). It can be observed that the competition effects on selected organic contaminants by FA followed in an order of nitrobenzene > amine organic contaminants > phenolic organic contaminants (Fig. 2a, Fig. S4). This could be attributed to the hydrogen-bonding donor ability (α_m) of these organic contaminants, suggested by the significant negative correlation between K_{f-b}/K_{f-m} and α_m at various FA concentrations (Fig. 2b). Because hydrogen bonding interaction plays an important role in adsorption organic contaminants by carbon materials [33,35,37,38]. α_m is an important parameter that can reflect the ability to form hydrogen bonding interaction between organic contaminants and carbon materials. Functional groups such as –COOH, –OH, and –NH$_2$ groups of organic contaminants can act as hydrogen-bonding donors, while the benzene rings on the surface of carbon materials can act as hydrogen-bonding acceptors [33]. The correlation between K_{f-b}/K_{f-m} and α_m of organic contaminants became stronger as the concentration of FA increased (Fig. 2b), which indicated that the adsorption capacity and affinity of organic contaminants with higher hydrogen-bonding donor ability tend to be less suppressed by the competition of FA. At a given FA concentration of 50 mg TOC/L, a high concentration level of DOM in natural water and soil water [39–42], adsorption of these selected organic contaminants in a wide concentration range (the relative equilibrium concentrations C_e/S_w ranged from about 0.0001 to 0.75) on KAC were not significantly suppressed by FA (Fig. 3a–g). As the average value of the competition suppressing rate $\Delta K_f/K_{f-m}$ (the ratio of reduced Freundlich affinity coefficient ΔK_f of organic contaminants with FA to K_{f-m} of organic contaminants in mono-component system) was lower than 5% (Fig. 3h), and the average value of K_{f-b}/K_{f-m} was higher than 0.95 (Fig. 3h). In addition, K_{f-b}/K_{f-m} of organic contaminants by KAC with FA (50 mg TOC/L) in this study were significantly lower than that of organic pollutants by other carbon materials with DOM ($\leq$50 mg TOC/L) reported in the literatures (Fig. S5, Table S4) [15,16,43–51]. Thus, adsorption competition of organic contaminants by FA on KAC was weaker than that on other carbon materials. In addition, DA model can also be well applied to fit isotherms of these organic contaminants with or without FA on KAC (Fig. S6), corresponding fitting parameters were summarized in Table S5. It can be observed that DA model showed a better fitting than Freundlich model, and gives more information for the adsorption process from the related parameters such as saturation adsorption capacity (Q^0) and adsorption affinity (E) (Table S3 and Table S5). Adsorption capacity of organic contaminants including nitrobenzene, phenols and anilines by KAC, even with the addition of 50 mg TOC/L FA, can be up to 1100 mg/g (Table S5), which was about 3 times higher than that on other carbon materials reported in the literatures [7,37,38,52] (Fig. 4a). Meanwhile, the adsorption of FA at 50 mg TOC/L by KAC in binary-component systems was not obviously affected by organic contaminants as the adsorption amount of FA maintains about 106.92 mg TOC/g with or without organic contaminants (Fig. 4b), which is 3–5 times higher than other activated carbons and biochars reported in our previous research [27]. Moreover, adsorption isotherms of FA in mono-component system almost overlapped with those in binary-component systems with organic contaminants at 0.01 S_w and 0.1 S_w (Fig. S7). Combined with the isotherms (Fig. 1) and the adsorption of FA in mono-component and binary-component systems (Fig. 4b), it further indicated that organic contaminants in a large concentration would not affect the adsorption of FA on KAC. Therefore, KAC has a high adsorption capacity for FA coexisting with organic contaminants. This could be of great application significance for the simultaneous adsorption of FA and organic contaminants by KAC in practical environment, because FA is the most soluble component of soil DOM and easily lost into water. Due to the observed less competition and high simultaneous adsorption of organic contaminants and FA, KAC could be a promising adsorbent to simultaneously adsorb organic contaminants and FA in soil to reduce the risk of organic contaminants migration and the leaching loss of soil DOM.
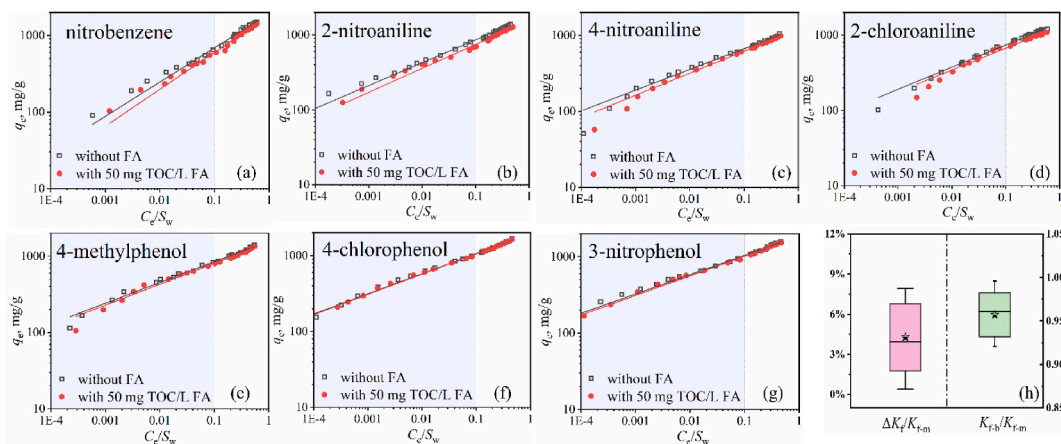

Fig. 3. Effects of FA (50 mg TOC/L) on isotherms of nitrobenzene, 2-nitroaniline, 4-nitroaniline, 2-chloroaniline, 4-methylphenol, 4-chlorophenol, 3-nitrophenol by KAC and on the competition suppressing rate ($\Delta K_f/K_{f-m}$) and the competition inhibition degree parameter (K_{f-b}/K_{f-m}).
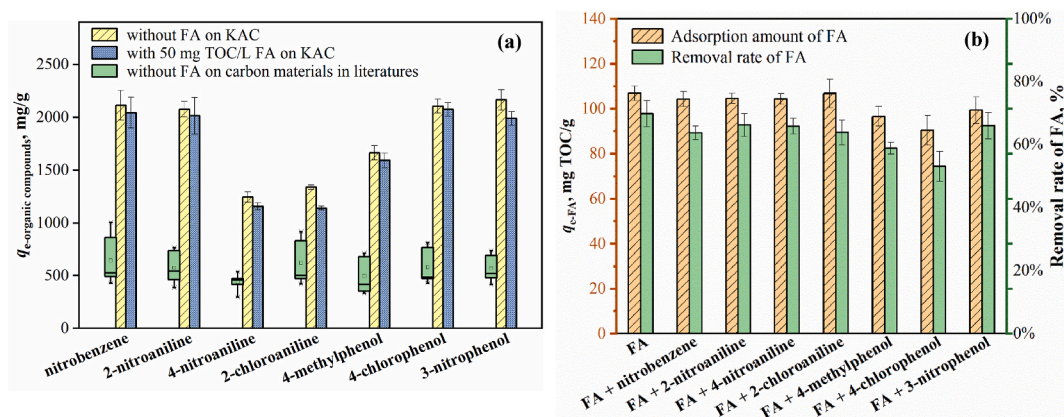
Fig. 4. Adsorption capacity of nitrobenzene, 2-nitroaniline, 4-nitroaniline, 2-chloroaniline, 4-methylphenol, 4-chlorophenol, 3-nitrophenol by KAC with or without FA, compared with that by the reported carbon materials without FA (a), and adsorption of FA ($C_{0\ FA}$ = 50 mg TOC/L) by KAC with or without organic contaminants (b).

3.2. Micropore blockage of KAC by FA

The surface properties and pore distribution of KAC after adsorbing FA (C_0 = 50 mg TOC/L) without organic contaminants in Fig. 4b were given in Table S6 and Fig. S8. It can be observed that the FA adsorbed KAC still possesses a high surface area (2234 m^2/g), micropores volumes (0.63 cm^3/g) and mesopores volumes (0.688 cm^3/g). The micropore volume of KAC has decreased by 34.6%, lower than the decrease of mesopore volume by the adsorption of FA, indicating that FA mainly occupied mesopores of KAC and has not completely blocked the micropores that are still available for organic contaminants. Thus, the low adsorption competition (Figs. 1 and 3) and high adsorption capacity of organic contaminants and FA (Fig. 4) on KAC could be explained by the different preferences of pore occupation between FA and organic contaminants. FA was more likely to be adsorbed in mesopores and macropores [17,18], as its average hydrodynamic diameter was reported as about 3.2 nm [53], while the hydrodynamic diameters of these selected organic contaminants are smaller than 2 nm [52], that can easily enter micropores. Therefore, KAC successfully conformed to the hypothesis that by expanding the pore size of adsorbent from micropores to mesopores as well as improving the proportion of mesopores could effectively reduce the adsorption competition between DOM and organic contaminants [8,15,16].

3.3. Adsorption sites competition on mesopores of KAC

Generally, organic contaminants at low equilibrium concentrations are mainly adsorbed in micropores with a high slope of the isotherm, while at high equilibrium concentrations, they tend to be adsorbed in mesopores with a low slope of the isotherm [7,23,37,
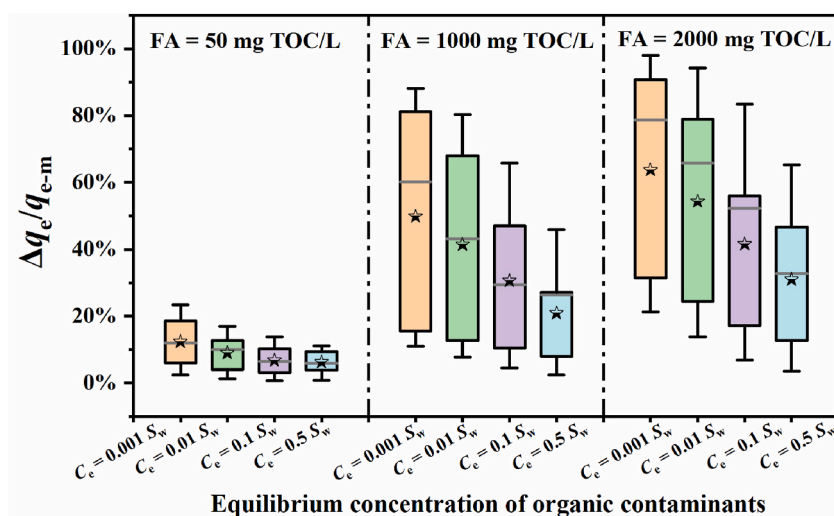

Fig. 5. Adsorption capacity decrease ratio $\Delta q_e/q_{e\text{-m}}$ with FA competition, calculated from DA model fitted equations of organic contaminants at the given equilibrium concentration C_e of 0.001 S_w, 0.01 S_w, 0.1S_w, and 0.5 S_w.

52].To determine the competition of organic contaminants at different equilibrium concentrations by FA and to explore the difference of competition between micropores and mesopores, the adsorption amount decrease ratio $\Delta q_e/q_{e-m}$ of organic contaminants at different equilibrium concentrations ($C_e = 0.001\ S_w$, $C_e = 0.01\ S_w$, $C_e = 0.1\ S_w$, $C_e = 0.5\ S_w$) by the competition of FA based on the fitted parameters obtained from DA model were analyzed (Fig. 5). At a given competitive concentration of FA, $\Delta q_e/q_{e-m}$ was decreased with an increasing equilibrium concentration of organic contaminants, and the decreases became more significant with higher competitive concentrations of FA. This indicated that organic contaminants adsorbed in mesopores at higher equilibrium concentrations were less suppressed by FA than those adsorbed in micropores at lower equilibrium concentrations. Subsequently, KAC with a high mesopore volume (1.284 cm^3/g) could provide more adsorption sites on mesopores for organic contaminants in large concentrations even with the competition of FA. Thus, the good performance of weak adsorption competition and high simultaneous adsorption capacity of organic contaminants and FA can also be attributed to the weak adsorption site competition on mesopores of KAC.

3.4. Heterogeneous nature of hydrophilic sites on KAC's surface

With increasing initial concentration of FA, the adsorption capacity and affinity of organic contaminants on KAC were decreased to different degrees (Fig. S4 and Fig. S9). To explore the reason for the different effects of FA on the adsorption of selected organic contaminants by KAC, the physicochemical properties of organic contaminants in Table S1 with their adsorption capacity and affinity were analyzed. There were insignificant correlations between Q^0 and the maximum cross-sectional area (A, nm^2) of organic contaminants (Fig. S10a) with various FA concentrations, indicating that the adsorption of organic contaminants both in mono-component and binary-components systems were not controlled by the pore-filing mechanism with molecular sieving effect [45] present on most carbon materials [7,38,52]. Negative relationship of Q^0 with the melting points (MP, °C) was observed in mono-component system (Fig. S10b), which was in agreement with previous studies that the adsorption of organic contaminants was dependent on the packing efficiency and stacking density of molecules on KAC [23,54]. However, the correlation of Q^0 with MP was changed to weak negative with increasing FA concentration (Fig. S10b), indicating that the gradually increased competition of FA would affect the packing efficiency and stacking density of organic contaminants on KAC. Adsorption affinity of organic contaminants on KAC was mainly dominated by hydrogen-bonding interaction and hydrophobic effect derived from van der Waals force [23,52] with or without FA, suggested by the positive correlations between the E value and the hydrogen-bonding donor ability (α_m) of organic contaminants by the competition of FA at various initial concentrations (Fig. 6). The heterogeneous sites on KAC's surface, classified simply into three types including the most hydrophilic adsorption sites, the less hydrophilic adsorption sites, and the hydrophobic adsorption sites like other oxygen-containing carbon material [33,35,55], could be employed to interpret the different competition among these organic contaminants (Fig. 7). The most hydrophilic adsorption sites are almost occupied by the oxygen-containing functional groups and can adsorb polar organic molecules like amine and phenolic organic contaminants by strong hydrogen-bonding interaction, rather than FA with fewer functional groups per same molecular weight and nitrobenzene with no hydrogen-bonding donor ability ($\alpha_m = 0$). The less hydrophilic adsorption sites are some polarized electron-rich or depleted sites such as surface defects on KAC and can combine with both organic contaminants and FA by weaker hydrogen-bonding interaction and hydrophobic effect. The hydrophobic adsorption sites can adsorb organic contaminants and FA molecules dominated by hydrophobic effect with less hydrogen-bonding interaction and weaker adsorption affinity. Therefore, the adsorption sites competition between organic contaminants and FA mainly occurred on the less hydrophilic adsorption sites of KAC (Fig. 7). Organic contaminants with higher hydrogen-bonding donor ability and strong adsorption affinity can occupy more of the less hydrophilic adsorption sites on KAC surface with lower competition inhibition degree
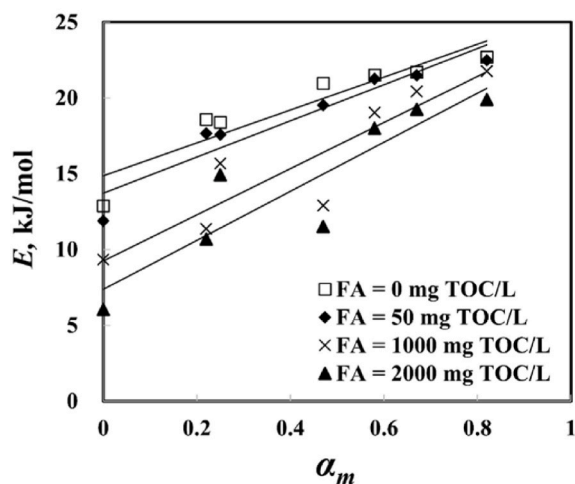

Fig. 6. Relationships between DA model fitted E value and hydrogen-bonding donor ability (α_m) of selected organic contaminants with FA at various initial concentrations.
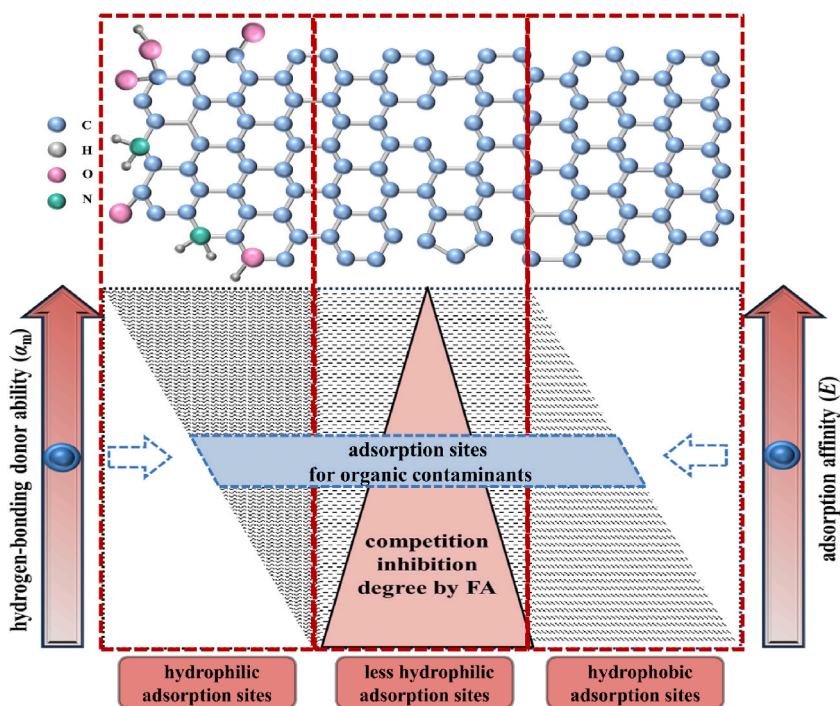
Fig. 7. Possible adsorption site competition of FA for organic contaminants with different hydrogen-bonding donor ability (α_m) and adsorption affinity on the KAC surface with heterogeneous sites including hydrophilic adsorption sites, less hydrophilic adsorption sites, and hydrophobic adsorption sites.

by FA.

3.5. Solubility enhancement of organic contaminants by FA

Early researchers have observed that DOM in water can enhance the solubility of many "hydrophobic" organic compounds like DDT and PCBs [11–14]. This can be accounted for the partition-like interaction of solute with DOM indicated by Chiou and co-workers [12]. They have determined the water solubility enhancement of some organic pollutants by dissolved HA and FA, reporting that with DOM less than about 50 mg TOC/L, the effect of DOM on solute solubility is minimal for relatively water-soluble solutes such as lindane (S_w = 7.3 mg/L) and 1,2,3-trichlorobenzene (S_w = 20 mg/L) [12]. Solubility enhancement of organic contaminants would reduce their adsorption on carbon materials, which is part of the negative effects of the coexisting DOM [56–60]. At the initial FA concentration of 50 mg TOC/L, the removal rate of FA by KAC was about 65% (Fig. 4b), leaving about 17.5 mg TOC/L FA remaining in the solution, lower than the reported 50 mg TOC/L [12]. In addition, organic contaminants employed in this study were relatively water-soluble ($S_w \geq 600$ mg/L) (Table S1). Thus, water solubility enhancement of these organic contaminants by FA on KAC was negligible.

4. Conclusion

Carbon materials, pyrolyzed from biomass, are increasingly suggested for organic contaminated soil remediation and carbon sequestration. However, the widely distributed DOM in soil and water environments will inhibit the adsorption of organic contaminants on carbon materials by competition and by enhancing contaminant solubility. The leaching loss of DOM from soil, especially FA (the most soluble component of DOM), will lead to a decrease in soil organic matter content as well as soil fertility. Here, we observed that the large surface area (3108 m^2/g) activated biochar KAC, with abundant micropores (0.964 cm^3/g) and mesopores (1.284 cm^3/g), can adsorb fulvic acid (FA) and organic contaminants (e.g., nitrobenzene, phenols, and anilines) simultaneously with weaker competition and higher adsorption capacity than other carbon materials. With 50 mg TOC/L FA, for example, the average competition suppressing rate ($\Delta K_f/K_{f\text{-}m}$) of organic contaminants on KAC was lower than 5%, the adsorption for organic contaminants and FA were higher than 1100 mg/g and 90 mg TOC/g, which is 3–5 times higher than that on other carbon materials reported in the literatures [7, 24,45–47] (Fig. 4a). Therefore, KAC could be an ideal adsorbent for both organic contaminants and DOM adsorption as well as carbon storage in soil.

4.1. Environment implication

Organic contaminants from pesticides, fertilizer, and other sources would cause significant threat to the soil environment and

human health. Carbon materials pyrolyzed from biomass are increasingly suggested for organic contaminated soil remediation. However, the widely distributed DOM will inhibit organic contaminants adsorption. Herein, a large surface area (3108 m^2/g) activated biochar KAC, with abundant micropores (0.964 cm^3/g) and mesopores (1.284 cm^3/g), can simultaneously adsorb DOM and organic contaminants (i.e., nitrobenzene, phenols, and anilines), with higher capacity and weaker competition than other carbon materials. This study provides a potential carbon material for organic contaminants retarding and carbon storage in soil.

Data availability

Data will be made available on request.

CRediT authorship contribution statement

Min Hu: Writing – review & editing, Writing – original draft, Visualization, Validation, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Wenhao Wu:** Writing – review & editing, Resources, Project administration, Investigation, Funding acquisition, Formal analysis, Data curation. **Chenkai Zhou:** Writing – review & editing, Validation, Formal analysis. **Hongxia Zhu:** Writing – review & editing, Validation, Formal analysis. **Laigang Hu:** Writing – review & editing, Validation, Formal analysis. **Ling Jiang:** Writing – review & editing, Validation, Formal analysis. **Daohui Lin:** Writing – review & editing, Resources, Funding acquisition, Formal analysis. **Kun Yang:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

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

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2024.e27055.

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