Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2019.23773

148 (2019) 195–201
April

Adsorption of phenanthrene on the magnetized biochar organiccoated by amphoteric modifier

Haixia He[a], Wenbin Li[a,*], Hongyan Deng[a], Le Kang[a], Run Qiu[a], Xuelian Li[a], Wei Liu[b], Zhaofu Meng[c]

[a]*College of Environmental Science and Engineering, China West Normal University, Nanchong, Sichuan 637009, China, email: amy-hehaixia@foxmail.com (H. He), Tel. +8608172568455, email: lwb062@163.com (W. Li), dhongyan119@163.com (H. Deng), kangle@cwnu.edu.cn (L. Kang), 15775817585@163.com (R. Qiu), 1047691586@qq.com (X. Li)*

[b]*Department of Natural Resource and Environment, Northwest A&F University, Yangling, 712100, China, email: lwmjp@163.com (W. Liu)*

[c]*Key Laboratory of Plant Nutrition and Agri-Environment in Northwest China, Ministry of Agriculture, Yangling 712100, China, Tel. +86 29 87080055, email: zfmeng@hotmail.com (Z. Meng)*

Received 16 August 2018; Accepted 12 January 2019

ABSTRACT

To explore the enhanced adsorption of phenanthrene on magnetized biochar (MC)organic coated by amphoteric modifier, co-precipitation loading by Fe_3O_4 was used to prepare MC. The MC was coated again by amphoteric surfactant dodecyl dimethyl betaine (BS-12) with different modification ratios (25%, 50%, 100%, 150%, and 200%). The adsorption and thermodynamic characteristics of phenanthrene on amphoteric-coated MC (BS-MC) were studied by batch method, and adsorption differences in temperature, pH value, and ionic strength were compared. The results indicated the following: (1) MC coated again by different ratios of BS-12 could enhance the adsorption capability of MC to phenanthrene. The adsorption capacity of phenanthrene by different BS-MC materials were ranked in the order of 25%BS+MC > 50%BS+MC > 100%BS+MC > C (biochar) > 150%BS+MC > 200%BS+MC > MC. The adsorption amount of phenanthreneon BS-MC materials decreased with increasing BS-12 coated ratio. (2) All BS-MC materials presented a negative temperature effect on phenanthrene adsorption at the range of 10–40°C and mainly showed a hydrophobic physical adsorption mode. The change in pH values caused no significant effect on phenanthrene adsorption of the different BS-MC materials. The adsorption amount of phenanthreneon the BS-MC materials all decreased initially and then increased with incresing ion strength, whereas the maximum adsorption amount appeared at the ion strength of 0.01 mol/L. (3) Henry equation could best describe the adsorption isotherms of phenanthrene, and phenanthrene adsorption on BS-MC materials was a spontaneous physical process characterized by decreasing enthalpy and increasing entropy.

Keywords: BS-12; Organic-coating; Magnetized biochar; Phenanthrene; Adsorption amount

1. Introduction

With the massive discharge of domestic sewage and industrial wastewater, the impact of organic pollutants on water environment progressively worsens [1]. Among these pollutants, persistent organic pollutants are stable, refractory, and exist in various environmental media for long periods, and they will eventually accumulate along the food chain and cause serious harm to human health [2]. Therefore, exploring the effective remediation technology of organic polluted water bears significance for protecting the water environment and human health.

Biochar has been widely studied and applied in the fields of pollutant treatment and water purification due to its porous

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*Corresponding author.

structure, large specific surface area, rich functional groups, and other characteristics and good adsorption of organic pollutants existing in water environment [3–6]. Previous studies had shown that the adsorption of polycyclic aromatic hydrocarbons (PAHs) by biochar is mainly a distribution effect and surface adsorption [7]. At the same time, the raw material, pore structure, and functional groups were directly related to the adsorption capability of biochar to PAHs [8–10]. Biochar had attracted considerable attention for its excellent adsorbability for pollutants, but its application is limited by the difficulty of separating it from water solutions [11]. Magnetizing biochar with magnetic medium is an effective method to solve this nonseparability problem, thus realizing solid–liquid separation under the action of magnetic field [12]. When Xi et al. prepared magnetic biochar by loaded Fe_3O_4 on biochar to verify its removal effect for pyrenein water, they discovered found that LZ1.5 (magnetic biochar, the number after letters was 1.5 g Fe_3O_4 according to the theoretical value of generated $Fe^{2+}+2Fe^{3+}\rightarrow Fe_3O_4$) presented the best adsorption effect on pyrene, and the maximum adsorption amount of pyrene reached 2758.60 mg/kg [13]. Compared with original biochar, the magnetic biochar contained more mesopores and better thermal stability, which are beneficial to the adsorption of macromolecular organics [14]. In addition, the magnetized biochar (MC) could be regenerated and recycled due to the desorption of organic pollutants [15].

Amphoteric modifiers possess both positive and negative charge hydrophilic groups and a hydrophobic carbon chain, which cannot only produce electrostatic adsorption to heavy metal ions but also form hydrophobic binding with organic pollutants. Previous studies had shown that the adsorption and fixation capability of amphoteric modified clays to organic pollutants considerably improved compared with unmodified clays [16–19]. Meng et al. used octadecyl dimethyl betaine (BS-18) to modify bentonite [20], the adsorption capability of phenol by the modified samples increased significantly and showed a trend of(according to the modified ratio) 150%BS-18 > 100%BS-18 > 50%BS-18 > 25%BS-18 > CK (bentonite) [21]. Li et al. observed that the modification of dodecyl dimethyl betaine (BS-12) on the soil surface remarkably promoted the hydrophobic binding of organic pollutants, showing that a larger modification ratio results in stronger adsorption capacity to phenanthrene [22,23], and that the adsorption mechanism is mainly hydrophobic adsorption. If the MC is subjected to organic coating treatment by adopting amphoteric modification, then the adsorption capacity of the MC to phenanthrene could be enhanced. Meanwhile, the biochar and BS-12 are cheap, easily available, and eco-friendly and causes no pollution in the water environment. These materials could notably alleviate the harm brought by organic pollutants to water, animals, plants, and microorganisms. At present, limited research results considering this aspect.

To verify the adsorption efficiency of amphoteric-coated MC to phenanthrene in water, the amphoteri MCs with different amphoteric coating proportions were prepared. The isothermal adsorption and thermodynamic characteristics of phenanthrene by different amphoteric MC were studied, and the effects of temperature, pH value, and ionic strength on phenanthrene adsorption were also discussed to provide theoretical basis for the application of amphoteric-coated MC in treating organic pollutants.

2. Materials and methods

2.1. Materials

Biochar, $FeCl_3·6H_2O$, $FeSO_4·7H_2O$, and phenanthrene (with purity higher than 95.0%) were all purchased from Chengdu Cologne Chemical Reagent Factory, Chengdu City, Sichuan province, China.

BS-12 was used as the amphoteric modifier and provided by Xingguang Auxiliary Factory, Tianjin City, Sichuan province, China.

2.2. Preparation of amphoteric MC

(1) Preparation of MC

A co-precipitation method was used to prepare MC [24]. In this method, 20.00 g biochar (C) was dispersed into 2.0 L distilled water and stirred for 30 min. Under the protection of nitrogen, 0.4 $MFeCl_3·6H_2O$ and 0.2 M $FeSO_4·7H_2O$ were successively added to 60°C water fully stirred for 2 h, and then heated to 75°C. Adjusting pH to 10 with 5 mol/L NaOH solution and after continuous stirring for 1 h, naturally cooling, the magnetic material was separated by magnets. MC could be obtained after washing several times with distilled water (dH_2O). Then, the MCs were dried at 60°C and then passed through a 60-mesh sieve.

(2) Preparation of BS-12-coated MC (BS-MC)

A wet process was used to prepare BS-MC [25]. In this process, 100 g MC was slowly added to 1.0 L dH_2O. Then, different ratios of BS-12 calculated according to the cation exchange capacity (CEC) of MC were added again. After stirring at 40°C for 3 h, the samples were separated by magnets. BS-MC could be obtained after washing thrice with dH_2O. BS-MCs were dried at 60°C for 12 h and then passed through a 60-mesh sieve. 25%, 50%, 100%, 150%, and 200%

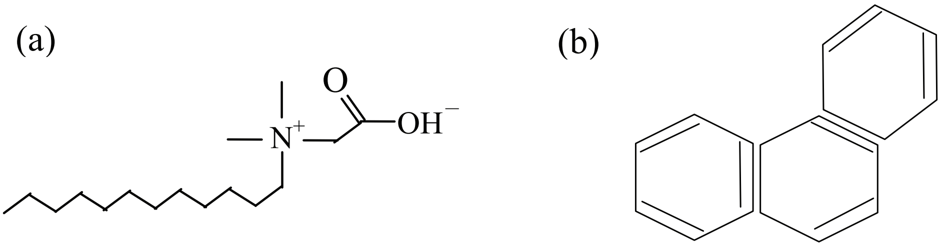

Fig. 1. Structural formula of BS-12 (a) and phenanthrene (b).

CEC BS-12-coated MC were prepared and recorded as 25% BS-MC, 50% BS-MC, 100% BS-MC, 150% BS-MC, and 200% BS-MC respectively.

The weight of BS-12 for a certain weight of MC can be obtained by Eq. (1):

$$W_{BS} = m \times CEC \times M_{BS} \times 10^{-6} \times R_{BS}/b \tag{1}$$

where W_{BS} (g) refers to the weight of BS-12, m (g) denotes the weight of MC that will be coated, CEC (mmol/kg) represents the CEC of MC, M_{BS} (g/mol) specifies the molecular mass of BS-12, R_{BS} stands for the modified proportion, and b is the product content of modifier (mass fraction).

2.3. Experimental design

In the following experimental design, each treatment included three repetitions.

(1) Isothermal adsorption experiment of phenanthrene

The concentration of phenanthrene was set to nine gradients: 0.01, 0.02, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, and 1 mg/L. The temperature, pH value, ionic strength were 25°C, 4, and 0.1 mol/L NaCl, respectively.

(2) Influence of environmental factors

The main environmental factors were temperature, pH value and ionic strength. The adsorption differences in temperature, pH value and ionic strength were compared.

The experimental temperatures were set at 10, 25°C and 40°C (the pH value of the initial solution was 4, and the ionic strength was 0.1 mol/L NaCl). The pH value of the initial solution was set at to 3, 4, and 5 (the initial solution temperature was 25°C, and the ionic strength was 0.1 mol/L NaCl). The ionic strength of the initial solution was set to 0.01, 0.1, and 0.5 mol/L NaCl (the initial solution temperature was 25°C, and the pH value was 4).

2.4. Experimental method

Approximately 0.0100 g of BS-MC was added to 50 mL plastic centrifuge tubes for nine repeats. In each plastic centrifuge tube, 20.00 mL of phenanthrene series solution was added, and the tubes were capped tightly. Under the conditions of 25°C and 150 rpm, constant temperature oscillation was carried out for 2 h (previous kinetic experiments showed that adsorption equilibrium was achieved at 2 h) [22]. The tubes were centrifuged at 4800 rpm for 15 min, and the supernatant was separated. The mass concentration of phenanthrene in supernatant was measured, and the equilibrium adsorption amount of each material was calculated by subtraction.

Table 1
Basic physicochemical characteristics of the tested materials

Materials	pH values	CEC (mmol/kg)	Specific surface areas (m^2/g)
C	9.15	176.20	1368.33
MC	8.88	150.34	408.69
25%BS-MC	8.24	105.32	310.42
50%BS-MC	8.01	88.27	224.60
100%BS-MC	7.25	66.21	100.80
150%BS-MC	7.00	41.37	69.83
200%BS-MC	6.82	35.20	48.22

Phenanthrene was determined by SP-2100 UV-VIS spectrophotometer, and a certain amount of supernatant was accurately placed in a 10 ml colorimetric tube. Determination was carried out at 254 nm (full wavelength scanning proved negligible effect of BS-12 desorbed at this wavelength in phenanthrene determination). The equilibrium concentration and adsorption amount of phenanthrene were calculated, and reagent blank experiments were conducted at the same time.

2.5. Data processing

(1) Calculation of equilibrium adsorption amount

The equilibrium adsorption amount was calculated as Eq. (2) [26]:

$$q = \frac{(c_0 - c_e)V}{m} \tag{2}$$

Here c_0 (mmol/L) and c_e (mmol/L) are the initial concentration and equilibrium concentration of phenanthrene in the solution, respectively. V (mL) is the volume of phenanthrene solution added. m (g) represents the weight of the tested materials. q (mmol/kg) denotes the equilibrium adsorption amount of phenanthrene on the tested materials.

(2) Fitting of adsorption isotherms

Henry model was used to fit the adsorption isotherms of phenanthrene [23], as defined by Eq. (3):

$$S = Kc \tag{3}$$

Here, S (mmol/kg) corresponds to the amount of phenanthrene adsorbed by the solid adsorbent. c (mmol/L) denotes the concentration of phenanthrene contained in the supernatant fluid, and K is used to characterize the partition coefficient of adsorbate between solid adsorbent and solvent. To a certain extent, K also indicates the binding capability of the adsorbate on solid adsorbent.

(3) Calculation of thermodynamic parameters

The parameter K in Henry model represents the apparent adsorption constant, which is equivalent to the equilibrium constant K_a. The thermodynamic parameter calculated by K_a is called the apparent thermodynamic parameter [17], and the calculation Eqs. (4)–(6) are as follows:

$$\Delta G = -RT \ln K \tag{4}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{5}$$

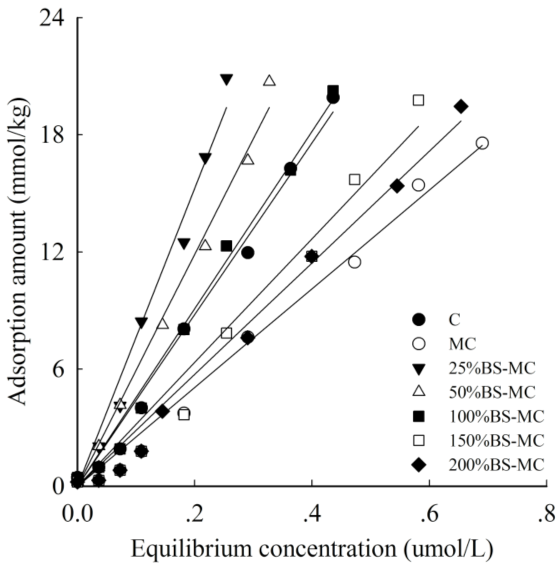

Fig. 2. Adsorption isotherms of phenanthrene on different tested materials.

$$\Delta H = R\left(\frac{T_1 \cdot T_2}{T_2 - T_1}\right)\cdot \ln\left(\frac{K_a, T_2}{K_a, T_1}\right) \tag{6}$$

The Curve Expert 1.4 fitting software was used in linear fitting, and Sigmaplot 10.0 software was adopted to improve data plotting.

3. Results and discussion

3.1. Adsorption isotherms of phenanthrene

Fig. 2 shows the adsorption isotherms of phenanthrene on C, MC, and BS-MC. The adsorption amount of phenanthrene on the tested materials all increased with increasing equilibrium concentration, showing linear adsorption characteristics. The adsorption capability of phenanthrene presented as 25% BS-MC > 50% BS-MC > 100% BS-MC > C > 150% BS-MC > 200% BS-MC > MC (*K* value in Table 3). Loading of Fe_3O_4 resulted in the significantly lower adsorption amount of MC to phenanthrene compared with that of C. After organic coating by BS-12, the adsorption amount of 25% BS-MC, 50% BS-MC, and 100% BS-MC to phenanthrene improved compared with C and MC. As a whole, the adsorption amount of BS-MC to phenanthrene decreased gradually with the increasing BS-12 coating ratio.

The adsorption capability of BS-MC to the organic pollutant phenanthrene was notably higher than that of MC, which indicating that BS-12 organic coating could significantly promote hydrophobic binding to phenanthrene. With the increase in organic coating ratio of BS-12, the adsorption amount of phenanthrene decreased gradually. This finding was mainly due to the covering effect of BS-12 hydrophobic carbon chains on the pores at the biochar surface. The larger proportion of BS-12 organic coated resulted in higher pore coverage by the hydrophobic long carbon chains on the biochar surface, which is non-conducive to phenanthrene adsorption [27].

Compared with the adsorption results of pyrene on magnetic carbon [13], the adsorption amount of phenanthrene on magnetized carbon was higher. This result is mainly due to the smaller size of phenanthrene molecules compared with pyrene molecules and less space resistance, which eases the achievement of adsorption point on the biochar surface.

3.2 Effect of temperature and ionic strength on phenanthrene adsorption

Fig. 3a shows that the adsorption amount of phenanthrene on different tested materials decreased with increasing temperature. The adsorption amount of phenanthrene on MC decreased by 17.22% as the temperature increased from 10°C to 40°C. The adsorption amount of C, 25% BS-MC, 50% BS-MC, 100% BS-MC, 150% BS-MC, and 200% BS-MC to phenanthrene decreased by 12.02%, 4.15%, 6.40%, 7.44%, 5.77%, and 12.69%, respectively. This result indicated that the effect of temperature on phenanthrene adsorption by BS-MC was connected with the organic coating ratios of BS-12. The above results were mainly due to the physical hydrophobic adsorption mechanism of the BS-MC materials, that is, a higher surface hydrophobicity of BS-MC resulted in greater adsorption of phenanthrene. This finding was consistent with Wan's research results on phenanthrene adsorption [24].

Fig. 3b shows that the adsorption amount of phenanthrene on each tested material decreased rapidly first and then increased with increasing ionic strength. The decrease in MC was larger than that in C and BS-MC. The adsorption amounts of 100% BS-MC and 200% BS-MC to phenanthrene reached the highest at anionic strength of 0.5 mol/L, increasing by 1.22% and 3.27% compared with that at 0.01 mol/L, respectively. However, for the other tested materials, the adsorption amount of phenanthrene was the highest when the ionic strength was 0.01 mol/L. This result was closely related to the structure and modification ratio of BS-12, where positive and negative charges existed between the carbon layer and BS-12 hydrophilic group on the surface of C and MC, respectively, thus hindering the adsorption of phenanthrene. However, the addition of background ions during neutralization of electrical properties remarkably promoted the combination of organic pollutants and organic phase on the biocharsurface. For BS-MC, the organic phase formed by the hydrophobic carbon chain on the surface of biochar had presented a notable advantage and considerably influenced phenanthrene adsorption, whereas the addition of the background ion caused negligible effects. This finding was similar to the results of Bai et al. and Li et al. on their research on phenol adsorption by amphoteric-modified soil [28,29].

3.3. Effect of pH change on phenanthrene adsorption

Table 2 shows that in the pH range of 3–5, the different materials caused no significant effects on the adsorption amount of phenanthrene. The adsorption of phenanthrene by 100% BS-MC increased with increasing pH value of the solution. The adsorption amount of phenanthrene by C, MC, 25% BS-MC, and 50% BS-MC decreased first and then increased with increasing pH value. The adsorption amount of phenanthrene reached the minimum at pH = 4. However, for 150% BS-MC and 200% BS-MC, the adsorption amount of phenanthrene decreased with increasing pH value.

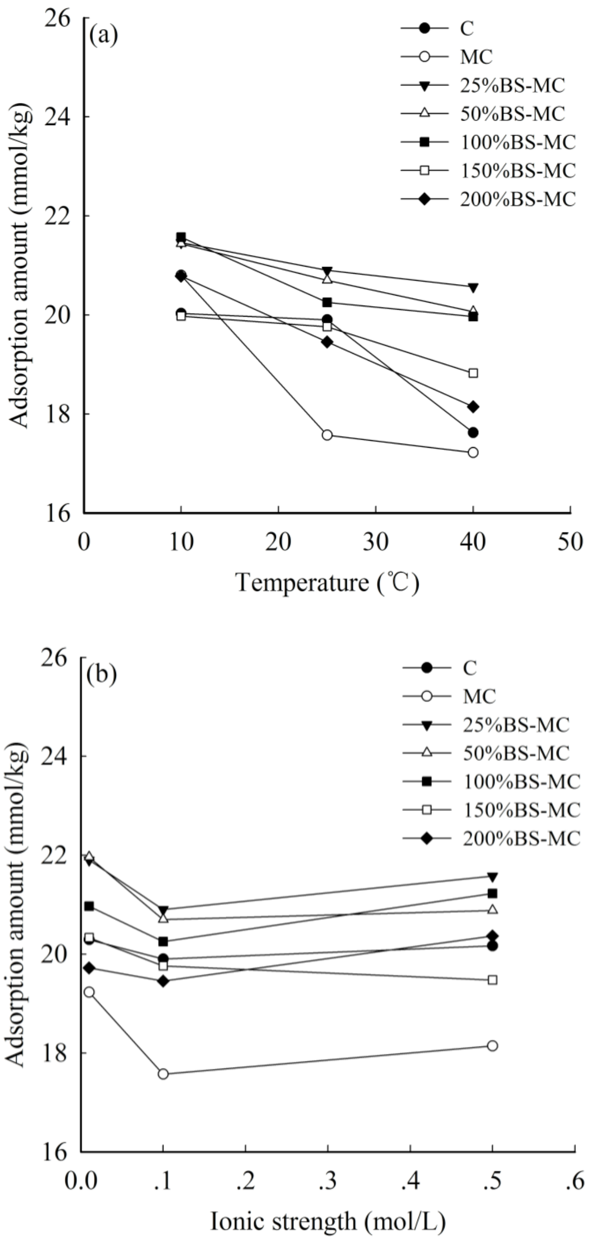

Fig. 3. Effect of temperature (a) and ionic strength (b) on phenanthrene adsorption.

For phenanthrene, the pH value of the solution caused no effect on its molecular form. The positive charge in the solution could neutralize the negative charge on the surface of alkaline biochar, thus benefitting the adsorption of phenanthrene. However, with the increase in pH value, the increase in OH^- would enhance the repellency to hydrophobic phenanthrene, thus reducing the adsorption amount of this compound.

3.4. Thermodynamic characteristics of phenanthrene adsorption

Table 2
Effect of pH value of solution on phenanthrene adsorption

Treatments	Adsorption amount (mmol/kg)		
	pH = 3	pH = 4	pH = 5
C	20.11±0.06a	19.90±0.11a	20.30±0.06a
MC	17.81±0.44a	17.57±0.09a	17.99±0.01a
25%BS+MC	21.91±0.52a	20.90±0.46a	21.85±0.23a
50%BS+MC	21.84±0.25a	20.70±0.40a	21.62±0.07a
100%BS+MC	20.18±0.10a	20.25±0.43a	20.96±0.23a
150%BS+MC	20.42±0.24a	19.76±0.15a	19.18±0.10a
200%BS+MC	20.13±0.17a	19.46±0.22a	19.32±0.24a

Note: The different lowercase letters indicate significant difference among treatments at 0.05 levels.

The parameters and thermodynamic characteristics of phenanthrene adsorption were fitted by the Henry model in Table 3, and the isothermal fitting of all tested materials to phenanthrene adsorption reached a highly significant level ($p < 0.01$). Under temperatures of 10°C and 40°C, the apparent free energy changes (ΔG) in phenanthrene adsorption in all tested materials were less than 0, indicating the spontaneous adsorption of phenanthrene. On the other hand, spontaneity was stronger at 40°C under the same treatment. The apparent entropy change $\Delta S > 0$, and the apparent enthalpy change $\Delta H < 0$ of the tested materials, showing the increasing exothermic and entropy adsorption processes. The results indicated the exothermic adsorption process of phenanthrene, which benefitted from the decrease in temperature. In other words, the adsorption of phenanthrene by all the tested materials was mainly physical adsorption and resulted in negative temperature effect. This conclusion was verified by the conclusion of the temperature effect mentioned above.

As shown in Table 3, from C to MC and to BS-MC, the value of $-\Delta G$ and ΔS had increased to different degrees, whereas the value of $-\Delta H$ had decreased in varying extent. The order of $-\Delta G$ was consistent with the distribution coefficient K fitted by Henry model in Table 3. The results confirmed that a greater adsorption spontaneity eases the adsorption of adsorbate on the adsorbent and larger equilibrium adsorption amount. Among the tested materials, the decrease in $-\Delta H$ and the increase in ΔS indicated that with the addition of organic modifier, the organic phase coverage on the biochar material increased, resulting in easier physical adsorption of phenanthrene. Therefore, the thermal energy required in the adsorption process decreased.

The increase in ΔS value was due to the increased surface coverage by the modifier on the surface of biochar material, resulting in increased adsorption sites on the surface of BS-12-coated MC material and multidirectional orientation of the molecular alignment of phenanthrene during the adsorption process. Numerous kinds of states were observed on the surface of BS-MC materials, and the degree of confusion increased, leading the increased entropy.

The adsorption of phenanthrene by biochar was mainly by distribution effect and surface adsorption. When Fe_3O_4 was loaded on the biochar surface, its surface pores became smaller and contained more mesopores, whereas the adsorption amount of the small-molecules phenanthrene reduced.

Table 3
Fitting parameters by Henry model and thermodynamic parameters of phenanthrene adsorption

Treatments	Fitting parameters			Thermodynamic parameters			
	Correlations/r	Standard deviations/S	K	ΔG_{10} (kJ/mol)	ΔG_{40} (kJ/mol)	ΔH (kJ/mol)	ΔS [J/(mol·K)]
C	0.9952^{**}	0.7266	43.97	–8.92	–9.53	–3.15	20.39
MC	0.9946^{**}	0.7049	25.28	–8.00	–8.36	–4.64	11.86
25%BS+MC	0.9892^{**}	1.1338	76.27	–10.27	–11.24	–1.04	32.57
50%BS+MC	0.9954^{**}	0.7323	59.32	–9.69	–10.55	–1.63	28.50
100%BS+MC	0.9950^{**}	0.7478	45.43	–9.13	–9.90	–1.90	25.54
150%BS+MC	0.9843^{**}	1.2934	31.70	–8.16	–8.87	–1.46	23.67
200%BS+MC	0.9936^{**}	0.8099	28.60	–8.05	–8.55	–3.34	16.65

Note: ** indicates that the correlation coefficient is significant at $p = 0.01$ level ($r = 0.765$ when the degree of freedom $f = 8$ and the level of significance $p = 0.01$).

Amphoteric modifier BS-12 contains both positively and negatively charged hydrophilic groups and hydrophobic carbon chains [25]. When BS-12 was loaded onto the MC surface, the BS-MC surface produced an organic phase, which was conducive to hydrophobic adsorption of phenanthrene. However, the long carbon chain of BS-12 also had gradually caused a covering effect on MC surface. Therefore, when the loading capacity of BS-12 was small, the adsorption amount of phenanthrene increased. However, given the large loading capacity of BS-12, the inhibition of its coverage was greater than its hydrophobic adsorption of phenanthrene, resulting in a decreased adsorption amount of phenanthrene, similar to the conclusion of Li et al. [22].

4. Conclusion

(1) BS-12 modification enhanced the adsorption amount of MC to phenanthrene. At 25°C, the adsorption amount of phenanthrene showed the following trend: 25% BS-MC > 50% BS-MC > 100% BS-MC > C > 150% BS-MC > 200% BS-MC > MC. Henry model was suitable to describe the isotherm of phenanthrene adsorption for all the tested materials.

(2) The adsorption of phenanthrene by BS-MC caused a negative temperature effect, and was mainly physical adsorption. The change in pH values showed no significant effect on phenanthrene adsorption. With the increase in ionic strength, the adsorption amount of phenanthrene for each tested biochar material decreased initially and then increased.

(3) Thermodynamic parameters showed that the adsorption of phenanthrene by biochar materials is a spontaneous and exothermic physical adsorption process. From C to MC and to BS-MC, the adsorption showed the characteristics of decreasing exothermicity and increasing disorder.

Acknowledgements

The authors wish to acknowledge and thank the Fundamental Research Funds of China West Normal University (17E057), the scientific research foundation of the education department of Sichuan province (18ZB0576) and the financial assistance from the scientific research foundation of Sichuan Science and Technology Agency (2018JY0224).

Conflict of intrests

The authors declare that they have no conflict of interest.

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