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Role of the functional groups in the adsorption of bisphenol A onto activated carbon: Thermal modification and mechanism

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Abstract: Surface properties of activated carbons play vital roles in adsorption of contaminants. Aiming to improve the adsorption of phenolic endocrine disrupting chemicals (EDCs), commercially activated carbon (W20) was modified via thermal treatment to obtain a carbon sample (W20N) with different characteristics. The content of acidic oxygen-containing groups of W20 was obviously reduced by the thermal modification. Bisphenol A (BPA) was chosen as the target compound. The adsorption results indicated that the acidic oxygen-containing groups (especially carboxyl groups) on the surface of activated carbons weakened the ability of carbon acting as π -donors that lead to the reduction of BPA adsorption. Compared to W20, W20N with greater number of phenyl groups exhibited higher adsorption capacity for BPA in a wide range of pH (4.0-10.0). Therefore, thermal modification improved BPA adsorption onto activated carbon. Furthermore, thermodynamic analysis and effect of solution pH revealed that BPA adsorption onto W20 and W20N probably followed face-to-face π - π dispersion interactions. And co-existing tannic acid (TA) formed BPA-TA complexes and played a negative role in BPA adsorption onto carbon based on the π - π dispersion interaction. This study should help broaden the scope of modification methods and the application of activated carbons to enhance the removal of phenolic EDCs.

Keywords: Adsorption; Activated carbon modification; Bisphenol A; Functional groups; Tannic acid

Introduction

Phenolic endocrine disrupting chemicals (EDCs) can mimic the biological activity of natural hormones and interfere with the reproductive systems of wildlife and humans. Such chemicals have been frequently detected in aquatic environment (Bolong *et al.* 2010). Thus, the issue of phenolic EDCs in aquatic environments has been of great concern in recent years (Zheng *et al.* 2015).

Many approaches have been attempted to remove phenolic EDCs from water. The adsorption by activated carbon is generally considered to be an efficient methods to control organic contaminants. Accordingly, some studies on activated carbon adsorption of phenolic EDCs have been explored. These researches are mainly focused on adsorption efficiency (Laatikainen *et al.* 2014), solution chemistry and properties of activated carbons (Bautista-Toledo *et al.* 2005). It is widely recognized that the properties of activated carbons, especially the surface acidic oxygen-containing groups, play significant roles in the adsorbability and adsorption mechanism of aromatic compounds (Vidal *et al.* 2015). On one hand, acidic oxygen-containing groups can decrease the adsorption of phenolic compounds arising from the π - π dispersion interaction between the aromatic ring electrons of the adsorbate and the basal plane electrons on activated carbon (Mahajan *et al.* 1980). On the other hand, these groups may be advantageous to the adsorption of phenolic compounds by hydrogen bonding interactions between hydroxyl groups of the target compounds and acidic oxygen-containing groups on activated carbon (Jung *et al.* 2013). The complex role of functional groups on the surface of activated carbon in adsorption and mechanism processes indicates the specificity for certain type of pollutants, and thus the modification carried out on activated carbon should depend upon the properties of target compounds accordingly.

Thermal treatment (Menéndez *et al.* 1996) and oxidation modification (Lu *et al.* 2012) are two effective ways to modify the surface functional groups on the surface of activated carbon. Jung *et al.* (2013) found the thermally treated biochars with more acidic oxygen-containing groups showed higher adsorption capacity for phenolic EDCs (Bisphenol A (BPA) and 17- α -ethinylestradiol (EE2)) compared to thermal oxidation modified biochars and high performance GAC. Furthermore, the adsorption activity might be attributed to H-bonding interaction and π -H-bonding interaction from acidic oxygen-containing groups (H-bonding acceptor) on the adsorbent. Sun *et al.* (2011) also reported the hydrothermal oxidation biochars with diverse oxygen-containing functional groups represented higher adsorption capacity of phenolic EDCs (BPA and EE2) as compared to the thermally treated biochars with low H/C and O/C ratios.

The research of Bautista-Toledo *et al.* (2005), nevertheless, revealed the adsorption of BPA onto activated carbons was mainly based on π - π dispersion interaction and the content of acidic oxygen-containing groups was possibly not the key to controlling the adsorption process. In addition, it was also reported that the more acidic oxygen-containing groups originated from nitric acid oxidation of activated carbon was unfavorable for the adsorption of BPA (Liu *et al.* 2009). Obviously, the specific effect of acidic oxygen-containing groups on the removal of phenolic EDCs remains ambiguous due to limited research in this area. Therefore, the in-depth mechanism, based on the change of surface functional groups of activated carbon, still needs to be further explored which may explain the adsorption of phenolic EDCs onto activated carbon.

It is well known that adsorption onto activated carbon (esp. granular activated carbon, GAC) has obvious advantages as they have high efficiency, easy operation, and no by-products. Currently, activated carbon have been well applied in removal of pollutants in water, such as halogenated nitrogenous disinfection by-products (Chu *et al.* 2012,), natural organic matter (Treguer *et al.* 2010), taste and odor (Qasim *et al.* 2000), bacteria (*et al.* 2000), and so on, during drinking water advanced treatment process and point-of-use filter system. However, a major problem of the application is that activated carbon exhibit the poor selectivity for some toxic contaminants (Bautista-Toledo *et al.* 2005). To the best of our knowledge, few literature reported the improvement of activated carbon adsorption applied in the pollution remediation of phenolic EDCs.

The objectives of this study were, using bisphenol A (BPA) as a representative of phenolic EDCs, to investigate (i) the effect of thermal modification on the surface properties of activated carbon, (ii) the adsorption characteristics of BPA onto two activated carbons with different surface properties (pristine carbon sample and modified carbon sample), (iii) the effects of temperature, solution pH and competition of TA on the adsorption of BPA onto the two activated carbons, and (iii) the adsorption mechanism.

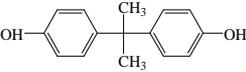
Materials and Methods

Materials

Bisphenol-A (BPA, 99+% purity) and tannic acid (TA) were purchased from Sigma-Aldrich. In view of the high value of $\log K_{ow}$ (3.32), the stock solution of BPA was prepared with methanol which was adsorbed slightly onto activated carbon in water (Giusti *et al.* 1974). The working solution of BPA was obtained by diluting the stock solution with pure water. Other reagents were of all analytical grades. The

character parameters of BPA are shown in Table 1.

Table 1 Character parameters of BPA

Molecular structure	
Molecular size / nm	Width: 0.94, Depth: 0.53, Thickness: 0.43 (Bautista-Toledo <i>et al.</i> 2005)
Molecular Weight / g·mol ⁻¹	228.29
Acid dissociation constant (pKa)	9.6-10.2
Water solubility /mg·L ⁻¹	120
Octanol/water partition coefficient (logK _{OW})	3.32

A commercially wood-based granular activated carbon (GAC) WV A1100 (Westvaco, Corp., American) was used and denoted as W20. The particle size of W20 was 0.4-0.8mm. The pristine carbon sample was washed using deionized water to an invariable solution pH value and desiccated at 378K for 24h. About 9g of sample W20 was placed in a fused silica tubular reactor. Thermal treatment was carried out for 3 hours under N₂ flow (100mL min⁻¹) at 873 K, and the modified sample was obtained and termed as W20N. More details about material and treatment could be found in our previous study (Liu *et al.* 2009). W20 or W20N (0.01g) was placed in a series of concical flask containing 100mL of TA solution (90mg·L⁻¹) with an ionic concentration of 0.1M (NaCl). The flasks were shaken continuously on an orbital shaker (150 rpm) in a thermostatic chamber at 298K. After 5 days, the modified activated carbons were filtrated and washed with deionized water to remove free TA, and then dried at 378K for 24h. Finally, they were designated as W20-TA and W20N-TA, respectively.

Characterization of activated carbons

Textural characterization for the carbon samples were determined by N₂ adsorption at 77K with an Autosorb-1-C automatic adsorption apparatus (Quantachrome, America). Brunauer-Emmett-Teller (BET) equation and density functional theory (DFT) were applied to analyze the data. The pH of point of zero charge (pH_{pzc}) of activated carbon was determined by using the method of Noh *et al.* (1989). The surface functional groups and basic sites were established by Boehm titrations (Boehm 1966). The elemental content of C, N and O onto the carbon samples was analyzed with a PHI5700 electron spectroscope for chemical analysis.

Adsorption experiments

For the isotherms studies, carbon sample (0.01g) was placed in 250mL conical flask containing 100mL of BPA solution (20-90mg·L⁻¹) containing 1mM phosphate buffer solution (pH 7.0). The flasks were shaken continuously on an orbital shaker (150 rpm) in a thermostatic chamber at 298K. Equilibrium was reached after 4 days. Keeping the initial conditions, the effects of temperature, solution pH and TA on the adsorption of BPA were investigated. The pH of the solution was adjusted using 1.0 mM phosphate buffer solution (pH 3.0-8.0) or 1.0 mM borate buffer solution (pH 9.0-11.0). The effect of TA was conducted through competitive adsorption between BPA and TA from aqueous solutions containing 60mg·L⁻¹ of BPA and variable TA concentrations (0-60mg·L⁻¹). The study was carried out at 298K, pH 7.0 by using 1mM phosphate buffer solution at a NaCl concentration of 0.1M. Furthermore, to analyze the competitive adsorption effect of TA, the maximum adsorption capacities of BPA onto the two tested carbon samples and the preloaded-TA carbon samples (W20-TA and W20N-TA) were also investigated using the aforementioned system with a constant ionic concentration of 0.1M (NaCl).

The BPA uptake Q_{ads} (mg·g⁻¹) was calculated from Eq. (1),

$$Q_{ads} = \frac{(C_i - C_e) \cdot V}{m} \quad (1)$$

Here, V is the solution volume (mL), C_i is the initial BPA concentration (mg·L⁻¹), C_e is the equilibrium BPA concentration (mg·L⁻¹) and m is the weight of the dry activated carbon (mg).

Analytical method

The concentrations of BPA in filtrate separated by filtration using a 0.7µm fiberglass membrane (GF/F, Whatman) were analyzed by high-performance liquid chromatography (HPLC, Waters 1525) equipped with a dual wavelength ultraviolet detector (Waters 2487), and was determined at 280 nm. A Waters Symmetry[®]C₁₈ column (4.6 µm × 15 cm, 5 µm) was used to separate BPA where the mobile phase was methanol/water (70:30, v/v) at a constant flow rate of 1 mL/min. The TA concentration was measured in a Multi N/C 3100 analyzer (Analytik Jena AG, Germany).

Results and Discussion

Characterization of activated carbons

The N₂ adsorption-desorption isotherms and the pore size distributions of the tested activated carbons are shown in Fig. 1 and Fig. 2, respectively. The inset (Fig. 2) shows the pore size distributions ranging from 10 to 120nm for the tested activated carbons. The specific textural properties of the activated

carbons are reported in Table 2. The N_2 isotherms and the pore size distributions of the W20 and W20N indicate that the textural characteristics of W20 were not drastically changed by thermal treatment, agreeing with previous reports (Menéndez *et al.* 1996). The slight reduction of specific area and total pore volume of W20N might result from the collapse of some of the pore walls during thermal treatment. Table 2 indicates that the average pore diameter (APD) value of W20 was increased from 3.579 to 3.756 nm by thermal treatment. In addition, Fig. 2 also shows that W20 and W20N were composed of micropores and mesopores. The chemical characteristics of the W20 and W20N, including the oxygen-containing groups, the pH of point of zero charge (i.e., pH_{PZC}) and the elemental analysis are given in Table 3. These characterization results indicate that thermal treatment caused the decomposition of some of the acidic oxygen-containing groups (especially for carboxyl groups), which made the density of delocalized π electrons on the oxygen-free Lewis basic sites rise (Menéndez *et al.* 1996). As a result, the basicity of activated carbon was increased, and the pH_{PZC} value of W20 was changed from 4.95 to 6.87 after thermal treatment.

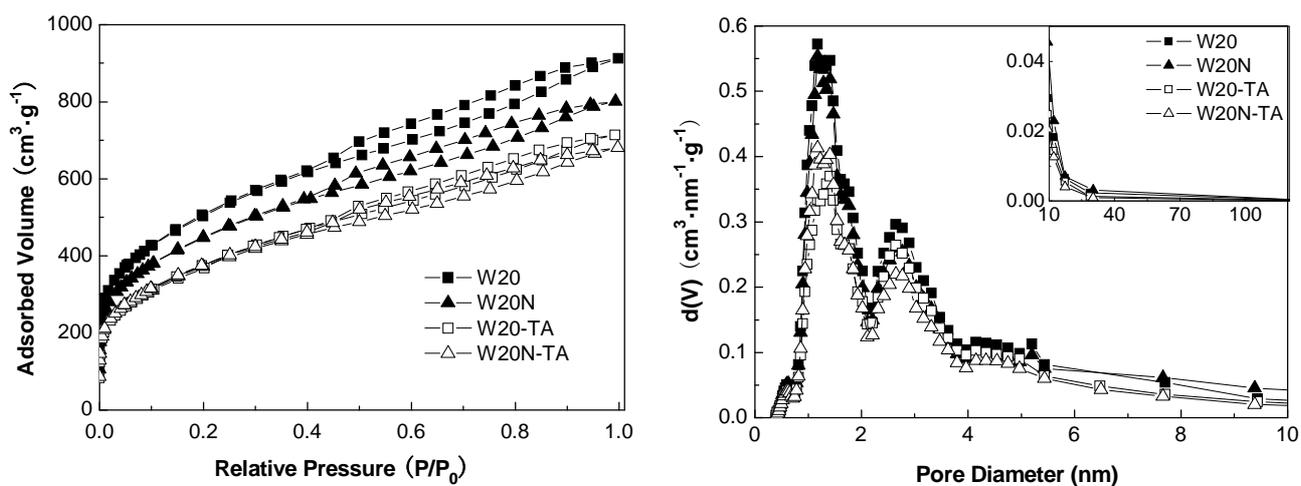


Fig. 1 Adsorption and desorption isotherms of N_2 onto activated carbons **Fig. 2** Pore size distributions of activated carbons

Table 2 Textural properties of activated carbons

Sample	S_{BET} ($m^2 \cdot g^{-1}$)	APD (nm)	TPV ($cm^3 \cdot g^{-1}$)	Pore volume distribution ($cm^3 \cdot g^{-1}$)		
				Micropore $d < 2nm$	Mesopore $2nm \leq d \leq 50nm$	Macropore $d > 50nm$
W20	1767	3.579	1.581	0.486	1.087	0.008
W20N	1669	3.756	1.567	0.456	1.103	0.008
W20-TA	1346	3.412	1.148	0.329	0.813	0.006
W20N-TA	1315	3.227	1.061	0.358	0.699	0.004

Table 3 Chemical characteristics of activated carbons

Sample	Hydroxyl group (mmol·g ⁻¹)	Lactone group (mmol·g ⁻¹)	Carboxyl group (mmol·g ⁻¹)	Basic sites (mmol·g ⁻¹)	pH _{PZC}	C (%)	O (%)	N (%)
W20	0.07	0.27	0.28	0.32	4.95	90.39	9.61	0
W20N	0.08	0.11	0.00	0.45	6.87	95.14	4.86	0

Adsorption isotherm

The adsorption isotherms of BPA onto W20 and W20N are shown in Fig. 3. The Langmuir and Freundlich models were employed to analyze experimental data, with the models shown in Eq. (2) and Eq. (3), respectively.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

$$q_e = K_F C_e^{1/n} \quad (3)$$

Here, q_e is the BPA uptake per unit mass of activated carbon at equilibrium (mg·g⁻¹); C_e is the equilibrium concentration of BPA in the bulk of solution (mg·L⁻¹); q_m is the adsorption capacity corresponding to the complete monolayer coverage of adsorption sites (mg·g⁻¹); K_L is the constant related to the free energy of adsorption (L·mg⁻¹). K_F and n are the constants related to sorption capacity and sorption intensity of the adsorbent.

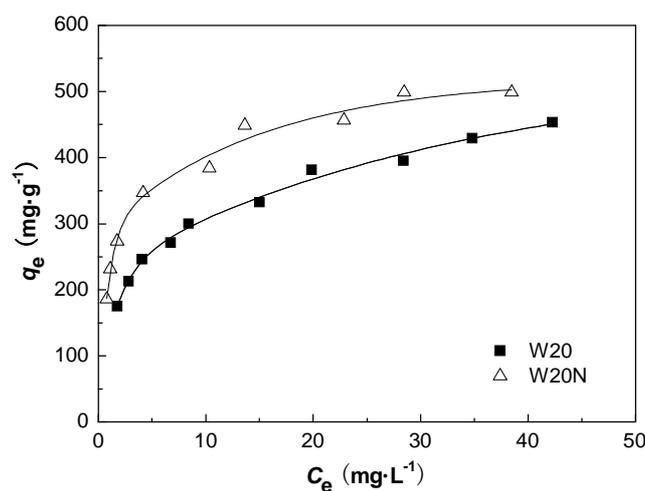


Fig. 3 Adsorption isotherms of BPA onto activated carbons at 298K and pH 7.0

The equilibrium isotherm constants of the above two models are shown in Table 4. The experimental data fitted to the Langmuir model better than to the Freundlich model, according to the higher value of R^2

obtained. Hence, this indicates the presence of a single-layer adsorption process, where the BPA interacted with the activated carbon surface throughout the adsorption process. Both W20 and W20N represented a high adsorption capacity to BPA. Especially, the adsorption capacity of W20N reached $526.32\text{mg}\cdot\text{g}^{-1}$ which was higher than that of W20. And the Langmuir constant K_L also indicated that W20N had a higher adsorption affinity to BPA than W20.

Table 4 Equilibrium isotherm constants of BPA adsorption onto activated carbons

Sample	Langmuir model constants			Freundlich model constants		
	$q_m(\text{mg}\cdot\text{g}^{-1})$	$K_L(\text{L}\cdot\text{mg}^{-1})$	R^2	K_F	$1/n$	R^2
W20	476.19	0.219	0.9916	157.67	0.284	0.9811
W20N	526.32	0.500	0.9961	223.77	0.239	0.9595

The thermal modification of activated carbon improved the adsorption capacity of BPA. Considering the slight change of structural properties between W20 and W20N, this may be due to the change of chemical properties on the surface of activated carbon before and after the thermal modification. Usually, the acidic oxygen-containing groups on activated carbons can adsorb more water molecules from solution to form water molecule clusters, which can prevent target organics from accessing the hydrophobic regions of the activated carbon surface. So, the more acidic oxygen-containing groups, especially carboxyl groups, on W20 (Table 3) could directly decrease the adsorption of BPA. This result is in agreement with other work investigating the effect of carbon surface acidity on the adsorption of some organic pollutants, such as phenol and nitrobenzene (Coughlin *et al.* 1968). Kim *et al.* (2011) also found that the acidic oxygen-containing groups and the organic moieties (phenyl groups) attached to the surface of adsorbents played a critical role in BPA adsorption.

Effect of temperature on adsorption

The effect of solution temperature on the removal of BPA was investigated in the range of 288K to 318K and pH 7.0. The adsorption isotherms are shown in Fig. 4. With an increase in temperature, the equilibrium uptake of BPA both decreased with W20 and W20N. The Langmuir model constants are given in Table 5. As the temperature increased from 288K to 318K, the adsorption capacities of BPA decreased from 500.25 to $429.74\text{mg}\cdot\text{g}^{-1}$ for W20 and from 532.47 to $468.76\text{mg}\cdot\text{g}^{-1}$ for W20N. This indicates that the low temperature is more favorable for the removal of BPA.

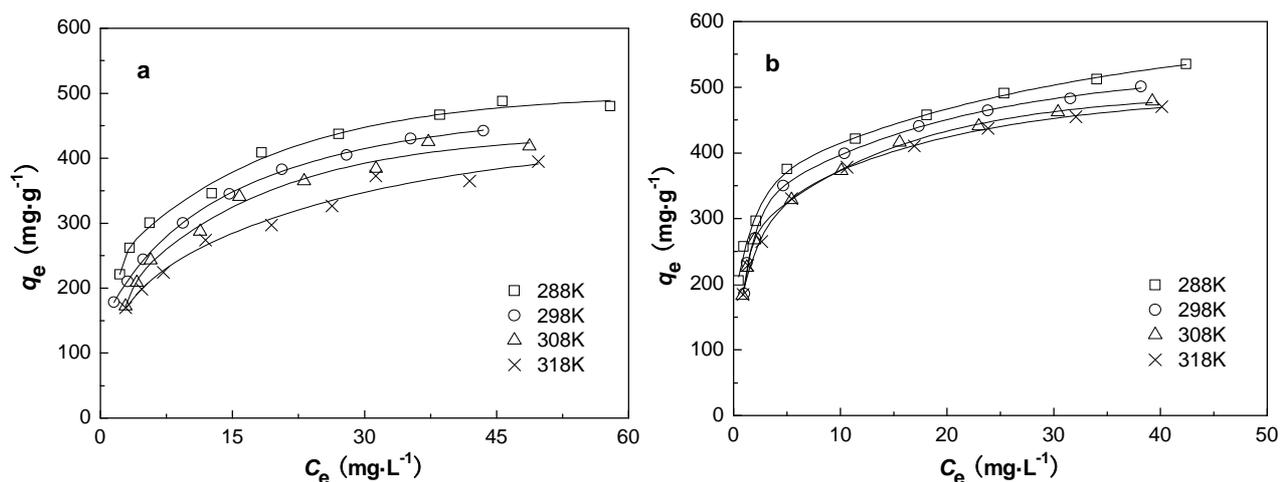


Fig. 4 Adsorption isotherms of BPA at different temperatures onto W20 (a) and W20N (b) at pH 7.0

The thermodynamic parameters can offer in-depth information on inherent energetic variations that relate to the adsorption. The Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) of BPA adsorption were calculated to analyze the thermodynamic behavior. These thermodynamic parameters were obtained from the following equations.

$$\Delta G = -RT \ln K_L \quad (4)$$

$$\ln K_L = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (5)$$

Here, K_L is the Langmuir constant at T ($L \cdot mmol^{-1}$); R is the universal gas law constant ($8.314 J \cdot mol^{-1} \cdot K^{-1}$); T is the solution temperature (K). The value of ΔH and ΔS can be directly obtained from the slope and intercept of the van't Hoff plots of $\ln K_L$ versus $1/T$, with relevant thermodynamic parameters being listed in Table 5.

Table 5 Thermodynamic parameters for BPA adsorption onto activated carbons at pH 7.0

T (K)	W20					W20N				
	q_m ($mg \cdot g^{-1}$)	K_L ($L \cdot mmol^{-1}$)	ΔG ($kJ \cdot mol^{-1}$)	ΔH ($kJ \cdot mol^{-1}$)	ΔS ($kJ \cdot mol^{-1}$)	q_m ($mg \cdot g^{-1}$)	K_L (L/mm)	ΔG ($kJ \cdot mol^{-1}$)	ΔH ($kJ \cdot mol^{-1}$)	ΔS ($kJ \cdot mol^{-1}$)
288	500.25	58.57	-26.29			532.47	141.77	-28.40		
298	476.19	50.89	-25.95	-12.51	47.93	526.32	127.16	-28.14	-8.55	68.94
308	458.30	41.85	-25.48			485.91	111.65	-27.83		
318	429.74	36.14	-25.13			468.76	101.82	-27.61		

The negative Gibbs free energy changes indicated that the adsorption processes of BPA onto W20 and W20N were both spontaneous. The absolute values of ΔG were decreased with the increasing temperature, which implies that the increasing temperature was detrimental to the adsorption process. The negative enthalpy change implies that the adsorption process was exothermic. Therefore, the amounts of BPA adsorbed were reduced by the increasing temperatures. The range of 40-120 $\text{kJ}\cdot\text{mol}^{-1}$ of enthalpy indicates a chemisorption mechanism, which is larger than that of physisorption (Hameed 2007). Hence, the enthalpy changes of $-12.51 \text{ kJ}\cdot\text{mol}^{-1}$ and $-8.55 \text{ kJ}\cdot\text{mol}^{-1}$ in this study means that the adsorption of BPA onto W20 and W20N is mainly based on physisorption.

Usually, the adsorption of adsorbates is accompanied with the desorption of water molecules and entropy changes can describe the interaction of the two processes. From Table 5, the entropy change of BPA adsorption onto W20 and W20N was $47.93 \text{ kJ}\cdot\text{mol}^{-1}$ and $68.94 \text{ kJ}\cdot\text{mol}^{-1}$, respectively. The entropy change of BPA adsorption onto W20N was larger, which could be attributed to the higher adsorption of BPA onto the modified carbon. To the best of our knowledge, water molecules are liable to form hydrogen bonds with the acidic oxygen-containing groups. Hence, water molecules were more easily released from W20N due to the less acidic oxygen-containing groups and the stronger hydrophobicity compared to W20, which promoted BPA adsorption and thus exchanged more water molecules. The entropy changes also indicated the detrimental effect of acidic oxygen-containing groups onto activated carbon samples for BPA adsorption.

Effect of pH on adsorption

The pH of solution is a key factor in controlling adsorbate adsorption in aqueous phase because it determines the charge of both carbon surface and adsorbate. The adsorption capacity of BPA was investigated onto W20 and W20N in the pH range of 3.0 to 11.0. Fig. 5 depicts the variations of saturated adsorption capacities (i.e., q_m) of BPA onto W20 and W20N with respect to the initial pH. Changes in the pH resulted in a minimal adsorption variation of BPA onto W20 (< 7%). W20 exhibited the best adsorption capacity (479.78 mg g^{-1}) at pH 5.0 and the worst (449.03 mg g^{-1}) at pH 11.0. Compared to W20, W20N represented higher adsorption capacity of BPA in a wide range of pH (4.0-10.0). The adsorption of BPA on W20N increased from pH 3.0 to 7.0 and then dropped from 7.0 to 11.0. The maximal adsorption of $526.32 \text{ mg}\cdot\text{g}^{-1}$ onto W20N occurred at pH 7.0 and the poorest adsorption capacity of BPA onto W20N was also observed at pH 11.0. However, the adsorption of BPA onto W20N was also more sensitive to the change

in pH due to the obvious change of adsorption with an increase in pH from 3.0 to 11.0.

The results were attributed to the degree of BPA dissociation and the net charge density of activated carbons derived from the surface acidic oxygen-containing groups at different pH values of the solution. The maximum values of BPA adsorption onto W20 and W20N were obtained near the pH_{PZC} of carbon samples (4.95 for W20 and 6.87 for W20N) where BPA is in its molecular state (Bautista-Toledo *et al.* 2005) and the activated carbons represents a surface charge density close to zero. Under these circumstances, π - π dispersion interaction and hydrogen bonding interaction could be strengthened. However, as the solution pH value exceeds neutral pH, BPA deprotonates and becomes a negatively charged species (Bautista-Toledo *et al.* 2005). At the same time, considering the pH_{PZC} of W20 (4.95) and W20N (6.87), the surfaces of the W20 and W20N will be negatively charged. Therefore, the electrostatic repulsion, occurring between BPA and carbon surfaces, weakened the adsorption interaction and reduced the adsorption capacity of BPA. Though the main form of BPA is the molecular state in the pH range of 3.0 to 7.0, the π - π dispersion interaction or hydrogen bonding interaction could also be weakened because of the existence of positive or negative charges on the surface of W20 and W20N (except the pH_{PZC} of activated carbons).

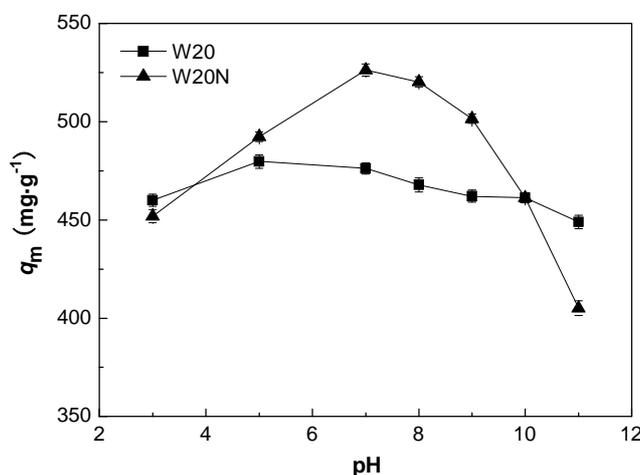


Fig. 5 Effect of solution pH on BPA adsorption onto activated carbons at 298K

Effect of TA on adsorption

The naturally occurring natural organic matter (NOM) has large amounts of phenyl groups and oxygen-containing groups in the molecular structure and affects the adsorption of organic compounds

onto activated carbon. Here, TA was selected as a model compound for NOM and its effect on the adsorption of BPA was investigated. The adsorption of BPA with various co-existing concentrations of TA (0-60mg·L⁻¹) onto W20 and W20N were carried out at an ionic strength of 0.1M at pH 7.0. With the adsorption of TA onto W20 and W20N, the surface characteristics of the samples might be changed and thus affect the adsorption of BPA in this competitive system. So, the adsorption of BPA onto W20 and W20N preloaded with complete TA coverage (i.e., W20-TA and W20N-TA) were also investigated at an ionic strength of 0.1M at pH 7.0. In the competitive system, the relative BPA uptake onto W20 and W20N is shown in Fig. 6. The q_0 and q is the amount of BPA adsorption in the absence and presence of TA in the solution, respectively.

As shown in Fig. 6, there was no obvious change in the relative BPA uptake (q/q_0) at a low concentration of TA (less than 2.5mg·L⁻¹). However, as the concentration of TA increased from 2.5 mg·L⁻¹ to 60 mg·L⁻¹, the q/q_0 values of two activated carbon samples were both decreased and the removal efficiency of BPA was reduced by 16.5% and 19.2% for W20 and W20N at 60 mg·L⁻¹ of TA, respectively. Obviously, the effect of co-existing TA was marked at a higher concentration of TA.

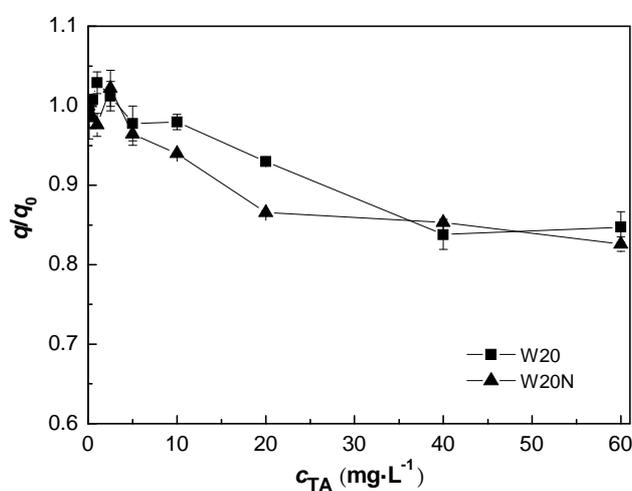


Fig. 6 Relative BPA uptake as a function of the TA concentration

There is likely to be two explanations for this effect. One is that the adsorption of TA onto W20 and W20N possibly leads to the changes of the surface characteristics of the carbon samples and thus decreases the active sites of BPA. The other is the formation of BPA-TA complexes. Considering that the surface characteristics change, W20 and W20N loaded with complete TA coverage, W20-TA and

W20N-TA, were characterized as shown in Fig. 2 and Table 2. It can be seen that the adsorption of TA reduced the specific area and total pore volume of W20 and W20N. The adsorption capacities of BPA onto W20-TA and W20N-TA are given in Table 6. The adsorption capacity of BPA onto W20 and W20N was only reduced by 3.71% and 9.22%, respectively, due to TA coverage. This was mainly attributed to the inaccessibility of TA to most of the micropore structures of the carbon samples due to the steric hindrance effect (Oćwieja *et al.* 2015), and thus BPA adsorption capacities were slightly decreased. This was consistent with the previous study on the effect of NOM preloaded for atrazine adsorption (Hopman *et al.* 1995). So the adsorption of TA could have a little influence on the active sites of BPA onto W20 and W20N. Hence, the formation of BPA-TA complexes might mainly be responsible for the reduction of BPA adsorption in competitive matrix. Yamamoto *et al.* (2003) reported that TA had a high sorption coefficient for endocrine disruptors with phenolic hydroxyl groups. Zhu *et al.* (2012) also discovered BPA-TA complexes played an important role in reducing the efficiency in adsorptive and extractive removal processes. The molecular size of BPA-TA complexes is much larger than that of BPA, and thus most of the micropores and mesopores of W20 and W20N may be impossible to access by the complexes. Additionally, the dissociation characteristics of BPA-TA complexes differ from BPA and may directly influence the interaction (esp. π - π dispersion interaction) between BPA and the surface of tested carbon samples. As a result, the formation of BPA-TA complexes obviously reduced the adsorption of BPA onto W20 and W20N in a competitive manner.

Table 6 Langmuir model constants of BPA adsorption onto activated carbons not preloaded and preloaded with a complete TA monolayer (298K, pH 7.0 and 0.1M in NaCl)

Sample	$q_m(\text{mg}\cdot\text{g}^{-1})$	$K_L(\text{L}\cdot\text{mg}^{-1})$	R^2
W20	500.01	0.220	0.9940
W20-TA	481.46	0.073	0.9957
W20N	529.10	0.388	0.9977
W20N-TA	480.31	0.125	0.9943

Adsorption mechanism

It is well known that the surface groups of the adsorbent can interact with the organic adsorbate and affect the adsorption of the latter. That means the hydrophilic and hydrophobic groups on the surface of activated carbons may interact with hydroxyl groups and organic moieties of adsorbate, respectively.

Similar interactions in the adsorption of alkylphenols and alkyylanilines on alkyl-grafted mesoporous alumina and silica were reported by Inumaru *et al.* (2006). Hence, BPA could also have two types of adsorbate-adsorbent interactions with W20 and W20N in this present study. One is of hydrogen-bonding interaction between the hydroxyl groups of BPA and the hydrophilic groups (such as carboxyl groups and hydroxyl groups) of the tested activated carbons. The other is of π - π dispersion interactions between the benzene rings of BPA and the phenyl groups of W20 and W20N. Based on the lower acidic oxygen-containing groups (Table 3) and higher BPA adsorption capacity (Table 4) of W20N, the adsorption mechanism of BPA onto activated carbon could be mainly based on π - π dispersion interactions. The possible adsorption manner is shown in Fig. 7.

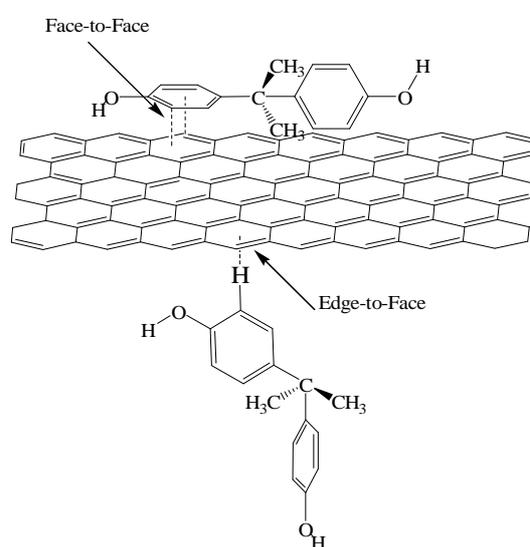


Fig. 7 Arrangement of π - π dispersion interaction between BPA and activated carbon

The π - π dispersion interaction could also be elaborated by the thermodynamic parameters. The value of $25 \text{ kJ}\cdot\text{mol}^{-1}$ of $-\Delta G$ was proposed as the evidence of π - π dispersion interaction that exist between π -acceptor and carbon sample by Zhu *et al.* (2005). In this study, the values of $-\Delta G$ (Table 5) close to $25 \text{ kJ}\cdot\text{mol}^{-1}$, therefore, the adsorption of BPA onto W20 and W20N should be mainly due to the π - π dispersion interaction. BPA had two adsorption forms on the activated carbon surface as depicted in Fig. 7. The positive values of ΔS in Table 5 suggest that the increase in ΔS from the desorption of water molecules was larger than the decrease in ΔS from BPA adsorption. It can be speculated that more water molecules were released from activated carbon samples to meet the BPA adsorption. So, the BPA molecular adsorption probably followed the face-to-face π - π dispersion interaction, which needs more

surface area (Fig. 7). The parallel π - π dispersion interaction also occurred between PAHs and NOM because NOM has similar molecular structures to activated carbon (Zhu *et al.* 2004).

Generally, the acidic oxygen-containing groups on the surface of the activated carbon sample can weaken the ability of carbon sample acting as π -donors (Keiluweit *et al.* 2009), and thus affect π - π dispersion interactions between activated carbon and BPA. The more phenyl groups on activated carbon are released, the better for BPA adsorption (Hu *et al.* 2009). Compared to W20, W20N had a greater number of phenyl groups, which enhanced the π - π dispersion interactions and made the BPA adsorption capacities of W20N more better and sensitive than that of W20 at the range of pH 4.0-10.0 (Fig. 5). Similar findings on the effects of acidic oxygen-containing groups on the adsorption of 4-nonylphenol (one of phenolic EDCs) onto multi-walled carbon nanotubes were also reported by Li *et al.* (2011). Furthermore, TA with a structural formula similar to the activated carbon samples was also engaged in π - π dispersion interaction with organic compounds carrying aromatic moieties (Keiluweit *et al.* 2009). From Fig. 6, the co-existing TA reduced the adsorption of BPA onto the tested carbon samples. Therefore, TA could act as π -donors and compete for BPA with carbon samples as result of forming BPA-TA complexes and decreasing the adsorption capacities of activated carbons. Considering the effect of BPA-TA complexes and the more stronger π - π dispersion interaction between BPA and W20N at pH 4.0-10.0, the effect of TA on the adsorption of BPA onto W20N was more serious (Fig. 7).

Conclusions

In this work, a commercially activated carbon, W20 was modified by thermal treatment under N_2 flow. Both the pristine and the modified W20 displayed high adsorption capacity for BPA. Langmuir isotherm model well describes the BPA adsorption onto two tested carbons.

The increase of temperature from 288K to 318K impaired the adsorption of BPA onto W20 and W20N. The best adsorption of BPA occurred at pH values close to the isoelectric pH values of the two tested carbon samples with the change of solution pH from 3.0 to 11.0, where the adsorption of BPA onto W20N was more sensitive than that onto W20. TA reduced the adsorption of BPA onto W20 and W20N by acting as π -donors and forming BPA-TA complexes.

The adsorption mechanism of BPA onto tested carbon samples was mainly due to the π - π dispersion interactions. However, the thermal treatment of activated carbon decreased the content of acidic oxygen-containing groups and thus increased the hydrophobic nature of carbon, resulting in the increase

in the adsorption capacity of BPA. The results further indicated that the acidic oxygen-containing groups on the surface of the carbon samples were unfavorable for the removal of BPA from aqueous solution. The results are expected to help broaden the scope of activated carbon modification to increase the removal efficiency of phenolic EDCs by activated carbon.

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