Adsorption and coadsorption mechanisms of Cr(VI) and organic contaminants on H₃PO₄ treated biochar

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H I G H L I G H T S

- H₃PO₄ treated biochar has much higher adsorption capacities than the untreated one.
- H₃PO₄ treated biochar can remove Cr(VI) and NAP (or BPA) simultaneously.
- The presence of Cr(VI) can increase the removal efficiency of BPA.
- Organic pollutants caused a limited decrease of removal efficiency of Cr(VI).
- High ionic strength does not affect removal efficiencies of Cr(VI), NAP and BPA.

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The study of simultaneous removal of heavy metals and organic contaminants has practical applications due to the coexistence of complex pollutants in the wastewater or soil. In this work, biochar was prepared to study the removal efficiencies of Cr(VI), naphthalene (NAP) and bisphenol A (BPA) in the single or mixed systems. H₃PO₄-treated biochar presented a much higher adsorption capacity of the pollutants than the untreated biochar and also showed a high resistance to coexisting salts. The maximum adsorption capacities for Cr(VI) and BPA were 116.28 mg g⁻¹ and 476.19 mg g⁻¹, respectively. Coadsorption experiments revealed that the presence of organic pollutants caused a limited decrease (~10%) of removal efficiency of Cr(VI) and no further decrease was observed with higher concentrations of organic pollutants, while the presence of Cr(VI) had little impact on the removal of NAP. Infrared spectra and molecular simulation demonstrated that Cr(VI) was mainly adsorbed on the biochar via chemical complexation, while the organic pollutants through π - π interaction. Unexpectedly, the addition of Cr(VI) increased the removal efficiency of BPA, probably due to the increased H-bond interactions between BPA and the biochar through bridge bonds of oxygenic groups from CrO₄²⁻.

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1. Introduction

Heavy metals and organic pollutants are two typical contaminants in wastewater and soils. United States Environmental

Protection Agency (USEPA) listed about 600 hazardous waste sites in 2011, which contain both heavy metals and organic contaminants (USEPA, 2011). In contaminated surface water and groundwater systems, Cr(III) usually coexist with bisphenol A (BPA) (Bautista-Toledo et al., 2014). When heavy metals and organic compounds coexist, they will probably interact with each other, and therefore cause a synergetic effect on human health and organisms (Koponen and Kukkonen, 2002). Among these heavy metals, Cr(VI) is an oxo-hydroxy anion that has a very high toxicity,

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solubility and mobility. Naphthalene (NAP), a nonpolar hydrophobic organic compound, is the smallest polycyclic aromatic hydrocarbon. It is often found in the groundwater and surface water in industry cities (Ramteke and Gogate, 2015). BPA used as plasticizer can cause adverse effects of endocrine disruptors on human beings and wildlife even at a low concentration (Wang et al., 2011), which exists in all types of environmental water. For these coexisting organic and inorganic contaminants in the environment, an effective remediation technology to simultaneously remove the hybrids is needed.

The methods including reduction, chemical oxidation, membrane filtration, precipitation/coagulation, solvent extraction, and adsorption are often used to remove heavy metal ions or organic compounds (Ramavandi et al., 2014; Gupta and Balomajumder, 2016). Amongst them, adsorption is the most promising technology because of its cost-effectiveness, simple operation and effective implementation. The adsorbent with high adsorption capacity and low cost is critical to remove pollutants in the adsorption process (Ahmadi et al., 2016).

Biochar, as a low temperature product of pyrolysis of biomass, is the material for the remediation of wastewater and soil. It has a high percentage of organic carbon structure with rich oxygen-containing groups, which can offer specific adsorption sites for heavy metal ions and aromatic contaminants. But normally its low surface area makes the adsorption capacity relatively low. Chemical activation of biochar by using a chemical agent can greatly enhance the surface area through the formation of well-developed porosity. The chemical agent of H_3PO_4 was chosen as the activation agent, because it is less corrosive and environmental hazardous. It also has higher chemical recovery efficiency than other agents (Guo and Rockstraw, 2007).

In recent years, considerable attention has been devoted to study the coadsorption mechanisms of heavy metal ions and organic pollutants. The coexistence of metal ions with organic pollutants will produce complex and diverse coadsorption mechanisms due to the interaction between the two adsorbates. For the binary system of Cr(III) and BPA, Cr(III) could act as central metallic cation and BPA, acting as ligand in the adsorption process to increase the adsorption capacities (Bautista-Toledo et al., 2014). But for CrO_4^{2-} anion, it could compete with orange II and orange G dyes (Darmograi et al., 2016). The coadsorption of lead ions and sulfa-pyridine on the carbon nanotube-modified biochar was site specific and there was no significant competition (Inyang et al., 2015). In the previous study, Chen and Wu (2004) found that the presence of humic acid (HA) could cause the enhancement of copper adsorption on activated carbon due to the formation of more organic functional groups in the HA-activated carbon. The adsorption mechanisms of heavy metals mainly include electrostatic attraction, surface complexation with functional groups, and reduction (Dong et al., 2011). On the contrary, the adsorption mechanisms of organic pollutants on biochar are more complex than that of heavy metals, which contain π -electron interaction (Zhu et al., 2005), condensation in capillary pores, multilayer adsorption, and partition (Chen and Chen, 2009).

Large quantities of agricultural biomass waste (e.g., corn straw) are produced in China annually. They are attractive feedstock for biochar production. In this paper, corn straw was selected as the raw material of biochar. In order to improve the inherent limit of the low surface area of biochars, H_3PO_4 was applied as the activation agent to modify the corn straw while keeping a relatively low pyrolysis temperature (300 °C). Brunauer-Emmett-Teller (BET)- N_2 surface area, scanning electron microscope, elemental analysis, and Fourier transform infrared spectroscopy were used to characterize the structural differences between the H_3PO_4 treated biochar and the unmodified biochar. The adsorption of Cr(VI), BPA and NAP on

the biochars was studied with the aim to understand: (1) the effects of surface areas and surface structure characteristics on the adsorption of organic and inorganic pollutants on H_3PO_4 treated biochar; (2) the effects of the presence of coexisting organic pollutants on Cr(VI) adsorption on H_3PO_4 treated biochar; (3) the effects of Cr(VI) on the removal efficiencies of nonpolar compound of NAP and polar compound of BPA.

2. Materials and methods

2.1. Materials

The air-dried corn straws were collected from Inner Mongolia, China. The chemical activation process of corn straw was carried out using phosphoric acid. In detail, dry corn straw (20 g) was impregnated with 35.6 mL 85% H_3PO_4 at room temperature for 24 h. According to our previous study, the biggest surface area of biochar appears at this biochar-to-solution ratio. Therefore, the same ratio was applied in the current study. In the following step, the impregnated sample was dried at 105 °C in the oven for 7 h. Then the dried impregnated sample as well as the untreated corn straw was placed in a stainless steel reactor (cylindrically shaped with a height of 10.5 cm and an inner diameter of 7.5 cm) and pyrolyzed in a furnace to heat up to 300 °C with the slow rate of 10 °C min^{-1} and held for 2 h. After that, both of the samples were washed respectively with 1 M HCl and 3 M HF followed by water till the electrical conductivity <18 $\mu\text{S cm}^{-1}$ to make sure that H_3PO_4 (in the chemical activated sample) and the ash materials were removed. The residues were ground to pass through a 0.21 mm sieve. The untreated corn straw biochar and H_3PO_4 treated biochar samples were referred to as C300 and H_3PO_4 -C300, respectively. Analytical-grade $\text{K}_2\text{Cr}_2\text{O}_7$ (>99.8% purity), NAP (>99% purity) and BPA (>99.7% purity) were obtained from Sinopharm Chemical Reagent Co., Ltd. The solubility of NAP and BPA at room temperature are 31.02 and 380 mg L^{-1} (Chen and Chen, 2009; Sun et al., 2011).

2.2. Characterization of biochars

Scanning electron microscope (SEM) was obtained using a Hitachi S-4800 scanning microscope (Japan) with a voltage of 3 kV. Pore and surface characteristics were tested by N_2 adsorption using an ASAP 2020 (Micromeritics, USA) surface area analyzer. Elemental compositions (C, H, N) were measured using a Vario EL III elemental analyzer (Elementar, Germany). Fourier transform micro infrared spectra (FTIR) were conducted in the region of 4000–650 cm^{-1} by a Spectrum Spotlight 200 FTIR spectrometer (PerkinElmer, USA) with the KBr-beam splitter and MCT/A detector. 32 scans were recorded in the absorbance mode at a 2 cm^{-1} resolution. All the FTIR spectra were normalized before the analysis.

2.3. Adsorption experiments

Batch experiments were conducted by adding biochars (18 mg for Cr(VI), 1 mg for NAP, and 10 mg for BPA) and 18 mL solution to a 50 mL glass vial. Cr(VI) with initial concentration ranged from 60 to 1050 mg L^{-1} at pH 7 was run to determine the adsorption isotherm. Each concentration point, including the blank and control samples was run in triplicate. The vials were placed in a shaker, agitated at 150 rpm for 24 h and centrifuged at 5000 g for 12 min. The solution and solid were separated by passing through 0.45 μm PTFE filter. The equilibrium concentrations of Cr(VI) were determined by measuring the absorbance of Cr(VI) with 1, 5-diphenylcarbohydrazide using a UV TU 1810 detector at 542 nm (Gupta and Balomajumder, 2016).

The stock solutions of NAP and BPA were prepared by dissolving in ethanol (the volume percentage <1%) and distilled water. NAP with initial concentrations of 5–65 mg L⁻¹ and BPA with the concentrations of 60–445 mg L⁻¹ were set to determine the adsorption isotherms. At the same time, 36 µL 200 mg L⁻¹ NaN₃ was added to prevent microbial growth. Each concentration point, including the blank and control samples was run in triplicate. The glass vials with Teflon screw caps were placed on a shaker and agitated in the dark at 150 rpm for 24 h. The solution and solid were separated by passing through 0.45 µm PTFE filter. The equilibrium concentrations of NAP and BPA were measured on UV detector at 222 nm and 276 nm, respectively (Chen and Chen, 2009; Wang et al., 2016a).

2.4. Data analysis

To insight into the adsorption mechanism of Cr(VI) by biochar, we performed computational study on the interaction of biochar with Cr(VI). Here, we used catechol as model to study the function of hydroxyl of biochar in removing Cr(VI). All the structures were optimized with hybrid density functional method B3LYP (Lee et al., 1988; Becke, 1993; Stephens et al., 1994) and 6-31 + G (d, p) basis set (Clark et al., 1983; Rassolov et al., 1998) in aqueous solution with Polarizable Continuum Model (PCM) solvation model (Miertuš et al., 1981). Frequency analyses were performed at the same theoretical level to verify that every structure was a local minimum in potential energy surface and to get the thermodynamic parameters. All the computations were performed with Gaussian 09 software (Frisch et al., 2010). The interaction energies were calculated according to the followed equation:

$$\Delta E = E(A^*B) - E(A) - E(B)$$

where $E(A)$ and $E(B)$ represent the energies of monomers, and $E(A^*B)$ is the energy of their interaction complex (Mousavi and Baghgoi, 2016). All the computational energy used in this paper are Gibbs free energy, the unit is kcal mol⁻¹.

2.5. Coadsorption experiments

To evaluate the coadsorption properties of H₃PO₄ treated biochar (H₃PO₄-C300), the removal efficiencies of Cr(VI), NAP and BPA in single and binary systems were conducted with 18, 1, and 10 mg adsorbent in 18 mL solution, respectively. For the competitive effect between heavy metal and organic compounds, individual removal efficiency of Cr(VI), NAP and BPA was also carried out. The initial concentrations were 20 mg L⁻¹ for Cr(VI), 65 mg L⁻¹ for NAP and 445 mg L⁻¹ for BPA. Each concentration point, including the blank and control samples was run in triplicate to eliminate the interaction between Cr(VI), NAP and BPA. The equilibrium concentrations of Cr(VI) were tested by measuring the absorbance of Cr(VI) with 1, 5-diphenylcarbohydrazide by UV detector with a UV wavelength 542 nm. The equilibrium concentrations of NAP and BPA in a single system were measured by the method mentioned above. The absorbance of NAP or BPA in binary systems was measured by UV detector with dual wavelengths 222 and 276 nm simultaneously. The equilibrium concentrations were calculated by using Vierordt's method according to the additive property of the absorbance (Abdel-Halim et al., 2016).

The effects of ionic strength on the removal efficiencies of pollutants in binary systems were studied. Different concentrations of NaCl solution (0.002, 0.02, 0.17, 0.34 M, respectively) were mixed with 10 mg adsorbent, 1 mg L⁻¹ Cr(VI) and 2.5 mg L⁻¹ NAP. The total volume of the solution was 18 mL. For another binary system of

1 mg L⁻¹ Cr(VI) and 4.5 mg L⁻¹ BPA, the added concentrations of NaCl solution were the same as above (Table S1).

3. Results and discussions

3.1. Characterization of the biochars

From the SEM images (Figs. S1a and b), it's clear to see that the surface morphology of biochar changes after activation by H₃PO₄. Corn straw biochar (C300) sample lacks the visible pores, while H₃PO₄-C300 consists of rough and irregular plates. The nitrogen adsorption and desorption isotherms of the biochars are presented in Fig. S1c. The adsorption and desorption branches of the isotherm for C300 remain nearly horizontal in the whole range of relative pressure, which indicates that nonporous or large macropores are formed. H₃PO₄-C300 shows a much larger surface area as compared to C300, and the average pore size of the former is smaller than the latter (Table S2). Elemental concentrations and atomic ratios of C300 and H₃PO₄-C300 are listed in Table S3. For H₃PO₄-C300, the C content increases from 61.67% to 69.03%, while the contents of O and N are reduced, indicating an increasing carbonization by H₃PO₄ activation. The lower H concentration and H/C ratio of H₃PO₄-C300 suggest that it is more aromatic than C300. The decreased O/C ratio of H₃PO₄-C300 reflects a more hydrophobic surface with lower amounts of oxygenated and acidic functional groups (Senesi et al., 2007). The small polarity index (O + N)/C of H₃PO₄-C300 demonstrates that few polar groups existing on the biochar (Wang and Chen, 2015).

FTIR spectra of C300 and H₃PO₄-C300 are shown in Fig. S1d. The broad bands around 3407–3430 cm⁻¹ can be attributed to the stretching vibration of OH groups in polymeric compounds (Reddy and Lee, 2014). The peak at 2931 cm⁻¹ of C300 is assigned to alkyl CH₂ stretching. The band around 1709 cm⁻¹ is due to the presence of aromatic carboxyl groups and the peaks at 1596–1612 cm⁻¹ represent aromatic C=C and C=O (Chen et al., 2011). The peaks at 1437–1450 cm⁻¹ correspond to aromatic C=C (Özçimen and Ersoy-Mericboyu, 2010). The bands observed at 1514, 1370, 1316, 1229–1266, and 1084 cm⁻¹ are C=C in guaiacyl lignin, C=O of carboxylated ions, hydroxyl bending vibration, OH in phenolic, C–O group in the alcoholic groups, respectively (Baldock and Smernik, 2002; Dong et al., 2011). Bands at 1162 cm⁻¹, corresponding to the OH bend (Bautista-Toledo et al., 2014). The bands at 835 cm⁻¹ and 757 cm⁻¹ are indicative of the aromatic compounds.

Changes in the function groups of corn straw biochar are visible after activation. In H₃PO₄-C300, hydroxyl is oxidized as suggested by the decrease of peak intensity at 3407 cm⁻¹ (Zhang et al., 2013). Aliphatic carbon is reduced as indicated by the disappearance of the peak at 2931 cm⁻¹ (Keiluweit et al., 2010), while the peak intensities of aromatic groups (1596–1612 cm⁻¹, 1437–1450 cm⁻¹, 835–757 cm⁻¹) are stronger than that of C300. This result is consistent with the elemental analysis. The loss of the signal at 1514 cm⁻¹ is due to the conversion of carbohydrate and lignin carbon into aryl structure (Baldock and Smernik, 2002). At the same time, all the peaks at 1709, 1370, 1316, 1266, and 1084 cm⁻¹ disappear, suggesting the content of oxygen-containing groups is reduced.

3.2. Adsorption isotherms

Adsorption isotherms of Cr(VI), NAP and BPA are shown in Fig. 1 and the data is fit with linear, Langmuir and Freundlich models (Table 1). In the concentration range, H₃PO₄-C300 has an enhanced adsorption capacity for Cr(VI), as compared with C300. Cr(III) is not detected in the solution. The data fits Langmuir isotherm well ($R^2 = 0.994$), suggesting that the adsorption is monolayer and the

Fig. 1. Adsorption isotherms of Cr(VI) (a), NAP (b) and BPA (c) by biochars. The lines represent the data fitted by the isotherm model. The bars are standard errors.

binding energy on the entire surface of $\text{H}_3\text{PO}_4\text{-C300}$ is uniform (Wen et al., 2016). The maximum adsorption capacity for Cr(VI) on H_3PO_4 treated biochar was 116.28 mg g^{-1} , which was higher than that of fox nutshell activated carbon treated by ZnCl_2 (Kumar and Jena, 2017). The experimental equilibrium result of Cr(VI) on C300 fits well with Freundlich isotherm, so it is multilayer adsorption and the adsorption heat is non-uniform distributed on the surface (Freundlich, 1906). Surface area and pore volume play vital roles in the adsorption process. $\text{H}_3\text{PO}_4\text{-C300}$ has very large surface area and pore volume, which provides more adsorption sites and makes the adsorption capacity larger than C300.

Adsorption isotherm of NAP on $\text{H}_3\text{PO}_4\text{-C300}$ is practically linear ($n = 0.9812$), which has a stronger linearity than C300 ($n = 1.274$). According to the previous research, adsorption isotherms of NAP on 150°C orange peels biochar (Chen and Chen, 2009), chitin, and cellulose (Wang and Xing, 2007) are also linear. The activation of H_3PO_4 makes the biochar exhibit very large surface area due to the carbonized process of biomass, which also leads to the non-carbonized organic matter degrades (2931 cm^{-1} band disappeared). Thus, $\text{H}_3\text{PO}_4\text{-C300}$ exhibits a higher adsorption capability than C300, mainly due to the strong $\pi\text{-}\pi$ interaction between NAP and the increased aromatic surface of $\text{H}_3\text{PO}_4\text{-C300}$ (Chen and Chen, 2009).

H_3PO_4 treated biochar exhibits excellent adsorption capacity for BPA, and the data fits Langmuir isotherm well ($R^2 = 0.993$). The adsorption of BPA increases rapidly with the increased initial BPA concentrations for $\text{H}_3\text{PO}_4\text{-C300}$. The modified adsorbent has a much higher maximal adsorption capacity of 476.19 mg g^{-1} due to its abundant micropores (the average pore size $\sim 2 \text{ nm}$), which probably increases the adsorption capacity by nanopore swelling (Cornelissen et al., 2005). This is even higher than the adsorption capacity of BPA (454.62 mg g^{-1}) on activated carbon developed from potato peels (Arampatzidou and Deliyanni, 2016).

The K_F value for the adsorption of BPA by $\text{H}_3\text{PO}_4\text{-C300}$ is higher than that of NAP and Cr(VI). So BPA has greater adsorption tendency towards $\text{H}_3\text{PO}_4\text{-C300}$ (Kose et al., 2012) as a result of the polar specific interaction (H bonding). After activation, isotherm shapes of the biochars have transition from Freundlich to Langmuir for Cr(VI), Freundlich to linear for NAP and linear to Langmuir for BPA, respectively. It is likely that the activation makes the adsorption of Cr(VI) and BPA take place at specific homogeneous biochar sites. Overall, the adsorption capacities of these three compounds are greatly increased, which can be attributed to the newly created surface area, porosity and functional groups.

3.3. Adsorption mechanisms

The mechanisms by which Cr(VI) are adsorbed onto biochars are examined using FTIR spectroscopy and quantum chemistry calculations. As shown in Fig. 2a, for Cr(VI) loaded biochar, the intensity of the band for the OH group at 3430 cm^{-1} increases, indicating the formation of H bond (Arampatzidou and Deliyanni, 2016). The increasing intensity of 1085 cm^{-1} indicates that the adsorption of Cr(VI) takes place on C–O groups. Moreover, the asymmetric Cr–O stretch vibrations of CrO_4^{2-} (885 and 821 cm^{-1}) appear after adsorption, proving that Cr(VI) forms the complexation with biochar (Johnston and Chrysochoou, 2015). Catechol is the pyrolysis product of corn straw biochar (Conti et al., 2016), so we use simple structure which contains catechol to represent biochar to interact with CrO_4^{2-} (Cr(VI) exists in the CrO_4^{2-} form in neutral solution). Then, we employ DFT methods to calculate the interaction energies of CrO_4^{2-} with catechol. The interaction energies of catechol with CrO_4^{2-} via the combination mode of surface complexation ($-5.15 \text{ kcal mol}^{-1}$) are stronger than that of H bond ($-3.56 \text{ kcal mol}^{-1}$). The calculated results are presented in Fig. 3a and b, where surface complexes and formation of H bonds between catechol and CrO_4^{2-} , respectively. Therefore, the calculated interaction energies indicate that biochar bind Cr(VI) mainly via surface complexation, where hydroxyl groups are the adsorption sites.

The microscopic mechanisms of BPA and NAP adsorption onto $\text{H}_3\text{PO}_4\text{-C300}$ can be further investigated by the FTIR measurement. For the adsorption of NAP (Fig. 2b), we can also confirm that aromatic C–H groups of NAP are adsorbed by biochar through the appearance of bands at $786\text{--}879 \text{ cm}^{-1}$. This $786\text{--}879 \text{ cm}^{-1}$ region belongs to fingerprint region of the FTIR spectra. Spectra in this region is extremely sensitive to changes in the molecular structure,

Table 1
Parameters for Cr(VI), NAP and BPA different adsorption isotherm equations.^a

Adsorbent	Compound	Linear $q_e = K_F C_e$ ^a		Langmuir $q_e = KaC_e/(1+KC_e)$			Freundlich $q_e = K_F C_e^n$		
		$K_F (L\ g^{-1})$	R^2	$K (L\ kg^{-1})$	$a (mg\ g^{-1})$	R^2	$K_F (mg\ g^{-1} (L\ mg^{-1})^{-n})$	n	R^2
C300	Cr(VI)	0.068 ± 0.002	0.957	0.601 ± 0.121	169.492 ± 32.683	0.790	0.179 ± 0.030	0.863 ± 0.032	0.980
H ₃ PO ₄ -C300		0.132 ± 0.004	-0.263	6.347 ± 0.405	116.279 ± 5.241	0.994	5.146 ± 0.243	0.453 ± 0.012	0.938
C300	NAP	15.549 ± 0.029	0.966	-16.362 ± 1.063	-588.235 ± 80.460	0.632	6.523 ± 0.444	1.274 ± 0.019	0.984
H ₃ PO ₄ -C300		24.449 ± 0.162	0.977	-1.412 ± 0.001	-16666.667 ± 8737.241	0.008	25.197 ± 0.296	0.981 ± 0.006	0.978
C300	BPA	0.278 ± 0.012	0.969	-0.481 ± 0.126	-500.000 ± 286.801	0.147	0.148 ± 0.020	1.119 ± 0.036	0.969
H ₃ PO ₄ -C300		3.026 ± 0.015	-0.842	59.155 ± 0.277	476.191 ± 0.000	0.993	87.510 ± 0.561	0.326 ± 0.001	0.980

^a q_e is the adsorbed amount at equilibrium. K_F , K and K_F are the partition coefficient, adsorption coefficient and Freundlich affinity coefficient, respectively. C_e is the equilibrium solution concentration. a is the Langmuir maximum capacity, and n is the Freundlich linearity constant (Inyang et al., 2015). Values are mean $\pm$ standard errors.

Fig. 2. FTIR spectra of H₃PO₄-C300 before and after reacting with Cr(VI) (a), NAP (b), BPA (c). (d) presents all the FTIR spectra in the range of 1000–2000 cm⁻¹. (The vertical lines are the guide for eyes.)

minor differences of the structures often lead to significantly different spectra. In Fig. 2c, after the adsorption of BPA, the band at 3430 cm⁻¹ shifts to the lower frequency 3386 cm⁻¹, indicates that H bonds are formed. At the same time, the peak at 3386 cm⁻¹ shortens after adsorption. This may be the involvement of carboxylic acid in BPA adsorption which leads to the breakage of O–H bonds (Devi and Saroha, 2015). The existence of the bands in the region between 761 and 880 cm⁻¹ of BPA loaded sample indicates that a certain number of aromatic C–H groups in BPA molecules have been adsorbed on the surface of H₃PO₄-C300. Furthermore, the band at 1229 cm⁻¹ shifts to 1247 cm⁻¹ after BPA adsorption, suggesting the interaction of these groups with OH groups of BPA through H bonding (Arampatzidou and Deliyanni, 2016). The increased intensity of 1442 cm⁻¹ also shows that the adsorption happens on aromatic C=C groups. The peaks at 2966, 2929, 1511, 1178 and 1016 cm⁻¹ appear after the adsorption, indicating the aliphatic methylene groups, C–O and O–H modes of phenol structures of BPA are adsorbed by biochars. After adsorption of

Cr(VI) and BPA, the bands at 1364–1386 cm⁻¹ appear and the peak intensities of 1697 cm⁻¹ increase may be due to the involvement of carboxylate groups in the removal of Cr(VI) and BPA (Sun et al., 2014).

Fig. 2d shows the zoom-in figures of FTIR spectra around 1605 cm⁻¹, and we can clearly see that the peak at 1596 cm⁻¹ shifts to 1605 cm⁻¹ and 1609 cm⁻¹ for NAP and BPA, respectively. This suggests that the adsorption mechanism is the π - π interactions between the π electrons of benzene rings of the biochars and those of NAP and BPA (Arampatzidou and Deliyanni, 2016). From the above results, we can see that the FTIR spectra of H₃PO₄-C300 are quite different before and after adsorbing BPA, and the adsorption sites are more complex than that of Cr(VI) and NAP.

3.4. Coadsorption of the Cr(VI)/BPA and Cr(VI)/NAP binary systems

The removal efficiency of each pollutant in the mixed systems was further investigated, with the aim of elucidating the interaction

Fig. 3. Calculated conformations of the surface complexes (a) and formation of H bonds (b) between catechol and CrO_4^{2-} . The dash lines are H bonds. Spheres with gray, white, blue, and red colours represent C, H, Cr, and O, respectively. These pictures were drawn with CYLview software (www.cylview.org). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 5. Schematic illustration of the adsorption of BPA on the biochar via the bridging CrO_4^{2-} . The dashed single line represents H bond.

between the two components during adsorption. As shown in Fig. 4a and b, in the absence of organic pollutants, the removal efficiency of Cr(VI) can reach 80% by $\text{H}_3\text{PO}_4\text{-C300}$. For the Cr(VI)/NAP and Cr(VI)/BPA systems, both NAP and BPA exhibit a certain competitive adsorption with Cr(VI) on $\text{H}_3\text{PO}_4\text{-C300}$, resulting in the removal efficiency of Cr(VI) decreasing to ~70%. But further increasing the concentration of BPA and NAP does not decrease the removal efficiency of Cr(VI). The results indicate that the competitive adsorption between organic pollutants and Cr(VI) is mainly from physical interaction. Comparing to hydrophilic inorganic ions, the hydrophobicity of organic pollutants shows their superiority in the physical adsorption on the biochar, due to the hydrophobic essence of the biochar surface. Therefore, the introduction of BPA and NAP leads to the loss of the adsorption of Cr(VI) by physical interaction (Meng et al., 2008). However, further increasing the concentration of the organic adsorbates will not decrease the removal efficiency of Cr(VI), which suggests that the two components occupy different chemical adsorption sites on the surface of the biochar.

Fig. 4. Removal efficiency of 20 mg L^{-1} Cr(VI) at different concentrations of NAP (a) and BPA (b), and of 65 mg L^{-1} NAP (c) and 445 mg L^{-1} BPA (d) at different concentrations of Cr(VI) by $\text{H}_3\text{PO}_4\text{-C300}$. The bars are standard errors.

Fig. 6. Removal efficiency of Cr(VI) (a) and NAP (b) in the binary systems of 1 mg L⁻¹ Cr(VI) and 2.5 mg L⁻¹ NAP, and of Cr(VI) (c) and BPA (d) in the binary systems of 1 mg L⁻¹ Cr(VI) and 4.5 mg L⁻¹ BPA on H₃PO₄-C300 at different concentrations of NaCl. The bars are standard errors.

The presence of Cr(VI) in the binary Cr(VI)/NAP system has little effect on the removal efficiency of NAP, as shown in Fig. 4c. It further confirms that Cr(VI) and NAP have different adsorption mechanisms. Cr(VI) is mainly interacting with oxygen-containing groups on the surface of the biochar, while NAP is adsorbed by π - π interaction with the aromatic groups on the biochars (Chen and Chen, 2009). Interestingly, when Cr(VI) and BPA coexist in the solution, the removal efficiency of BPA by the biochar increases with the increase of the concentration of Cr(VI), as shown in Fig. 4d. High linear correlation ($R^2 = 0.951$) between the removal efficiency and the initial concentration of Cr(VI) is observed. This can be attributed to surface complexation between biochar and CrO_4^{2-} , and then CrO_4^{2-} acts as the bridge bond to produce extra sites for attaching BPA via hydrogen bond interaction, such that the adsorption of BPA increases with the addition of CrO_4^{2-} . The schematic illustration is demonstrated in Fig. 5, it can be reasonably proposed that CrO_4^{2-} can interact with the OH groups of catechol by surface complexation and H-bond is formed between the O atom of CrO_4^{2-} and H atom in OH group of BPA.

The influence of ionic strength on the removal of the inorganic and organic pollutants is also checked and shown in Fig. 6. Normally, the presence of salt ions (e.g. Na^+ , NO_3^- , and Cl^-) in the waste streams may have adverse effects on the removal of metals and organic compounds due to competitive adsorption (Chen and Wu, 2004; Hu et al., 2005). However in our systems, the removal efficiencies of Cr(VI), NAP and BPA are not affected by the ionic strength of NaCl solution even at a very high concentration (~20000 times). This further reveals that the adsorption of the pollutants on H₃PO₄-C300 is proceeding by the aforementioned strong interface effects (Wang et al., 2016b). The adsorption of the pollutants from the salt solution with such a high concentration has never been reported, which might provide a novel method for treatment of the industrial wastewater with multicomponent pollutants and salts. Furthermore, our adsorbents show both an excellent regeneration

capacity in the removal of organic pollutants (BPA and NAP) and a high efficiency for the treatment of real wastewater leaching from chromite ore processing residue waste (See Text S1 and Figs. S2 and S3 in the supplementary material).

4. Conclusions

H₃PO₄ treated biochar presents significantly increase in the surface area and the enhancement of aromatic compounds, resulting in much higher adsorption capacities of both Cr(VI) and organic pollutants, as compared to the untreated one. It also exhibits a hybrid adsorption capacity to effectively remove heavy metal ions and organic pollutants simultaneously even with the existence of very high salt concentration. The presence of organic pollutants slightly decreases the adsorption of Cr(VI) via hydrophobic interaction, but does not show any further competition with Cr(VI) ions. The addition of Cr(VI) increases the removal efficiency of BPA through offering more adsorption sites via hydrogen bond interaction. The results reveal that Cr(VI) can be adsorbed on H₃PO₄-C300 by forming inner sphere complex with the surface oxygenic functional groups on the biochars, while the organic pollutants interact with the biochars by π - π and hydrogen bond interactions. The biochar we made shows a highly removal efficiency of pollutants and highly resistance to the salt coexisting in solution, which is potentially applicable into the remediation of the wastewater and contaminant soil.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.chemosphere.2017.08.016>.

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