Exceptional Adsorption of Phenol and *p*-Nitrophenol from Water on Carbon Materials Prepared *via* Hydrothermal Carbonization of Corncob Residues

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Phenol and *p*-nitrophenol (PNP) are priority pollutants widely present in wastewater. Developing superior or low-cost sorbents for their removal would be of great benefit. Here, corncob residues (CCR) were converted to hydrochars *via* hydrothermal carbonization (HTC) and further upgraded to carbon materials by thermal activation in an N_2 atmosphere. The influence of HTC conditions including the temperature, residence time, and CCR/water weight ratio on the material properties and their performance for removing phenol and PNP from water were investigated and compared with those that were obtained from pyrochar (directly pyrolyzed CCR). Hydrochars showed lower adsorption capacities for phenols than pyrochar. The initial hydrothermal treatment at 220 °C and 2 h resulted in an improved porosity and 4- to 5-fold higher adsorption capacities for phenol and PNP compared with the pyrochar. However, hydrochars prepared at 250 °C or with a prolonged residence time (4 and 6 h) could not be upgraded to high performance carbon materials by thermal activation. The adsorption isotherms of both phenols on the best performance material were well correlated by the Sips model.

Keywords: Hydrothermal carbonization (HTC); Corncob residues (CCR); Phenol; p-Nitrophenol (PNP); Adsorption; Carbon material

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INTRODUCTION

Phenol and *p*-nitrophenol (PNP) are priority pollutants widely present in many industrial effluents including but not limited to the petrochemical, pharmaceutical, coal, pulp and paper, steel, and food industries (Zhang *et al*. 2014). The concentrations of phenol and its derivatives in wastewater should be less than 1 ppm (mg/kg) (Busca *et al*. 2008). Therefore, the removal of phenols from water has attracted considerable attention, but it is still challenging due to their high stability and water solubility. Adsorption is a promising method for the removal of phenols, especially at low concentrations. Activated carbons (Dabrowski *et al*. 2005; Kumar *et al*. 2007) and polymeric resins (Pan *et al*. 2007; Huang *et al*. 2009; Lin and Juang 2009) are the most widely used adsorbents. Superior adsorbents with higher selectivity or low-cost adsorbents with satisfactory performance are still needed.

Biomass resources are plentiful, renewable, and not competitive to human and animal consumption. Making value-added products from agricultural lignocellulosic biomass waste is attractive in terms of cost and pollution management. It is economical to use agricultural waste biomass as precursors for carbon materials that remove phenols from wastewater. To date, various techniques have been applied to biomass treatment and conversion, including combustion, pyrolysis, and gasification.

Hydrothermal carbonization (HTC) uses water as the reaction medium to reduce the oxygen and hydrogen content of biomass at low temperature (150 to 350 °C) and self-generated pressure. Compared with thermal pyrolysis, HTC has the advantages of high conversion efficiency, less energy required by avoiding drying wet feedstocks, and relatively low operating temperatures (Hoekman *et al*. 2011; Guo *et al*. 2015). HTC can be carried out very quickly and is suited for a broader range of feedstocks because the initial moisture level is not an issue. HTC was recently used to fabricate functional carbon-based materials with applications in adsorption and separation science through processing waste biomass. Various biomasses have been converted to carbon materials through the HTC method (Titirici *et al*. 2007; Sevilla and Fuertes 2009a, 2009b; Calucci *et al*. 2012; Gao *et al*. 2013; Budai *et al*. 2014). HTC hydrochars normally need to be further upgraded to functional carbon materials *via* physical activation using an activating agent such as air, CO_2, or water steam (Román *et al*. 2013) or KOH chemical activation (Regmi *et al*. 2012; Falco *et al*. 2013*a*).

Corncob residue (CCR) is a waste lignocellulose. It has been exploited using HTC for various applications, such as high heating value biochar (Zhang *et al*. 2015), carbon precursors (Falco *et al*. 2013b), and soil fertility (Budai *et al*. 2014). In this work, HTC was used to convert CCR into hydrochars, and the hydrochars were further activated under N_2 by thermal heating to prepare carbon materials. The hydrochars and carbon materials were characterized. Their efficiency in the adsorptive removal of phenol and PNP was compared with the CCR pyrochar prepared by direct thermal pyrolysis without hydrothermal treatment.

EXPERIMENTAL

Materials

All chemicals used in this work were purchased from commercial suppliers and used without further purification. Absolute ethanol (AR grade), phenol (99.5%), and PNP (99.5%) were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). HPLC-grade methanol was supplied by Tedia Company Inc. (Fairfield, OH, USA). CCR was obtained from Zhejiang province, China. Prior to HTC, CCR was dried at ambient temperature, ground, and sieved. The particle size of 4 to 8 mesh (2.36 to 4.75 mm) was used to produce hydrochars.

Hydrothermal Carbonization Experiments

Either 5 or 10 g of CCR was weighed into a 100-mL PPL-lined stainless steel autoclave and then mixed with 40 mL of deionized water. The reactor was sealed airtight, heated from ambient temperature to the desired temperature, and maintained for varied times in an electric oven. The temperatures applied were 220 and 250 °C. After the preset residence time of 2, 4, and 6 h, the vessel was cooled to room temperature. Residence time was defined as the time the reactor was held at the desired reaction temperature, excluding preheating and cooling time. The hydrochar was recovered by centrifugation and washed twice with 25 mL of water, washed twice with 25 mL of ethanol, and then dried under vacuum at 100 °C overnight. The resulting hydrochar was named Hydrochar_X_Y_Z, where X, Y, and Z represented the HTC temperature (°C), residence time (h), and the solid/liquid weight ratio, respectively. The mass yield of hydrochars was calculated by the following equation:

$$\text{Solid mass yield}(\%) = \frac{\text{mass of dried hydrochar}}{\text{mass of dried raw CCR}} \times 100\% \qquad (1)$$

Hydrochar Activation

In the thermal activation process, the dried hydrochars were placed in quartz boats within a tubular furnace and heated from ambient temperature to 750 °C under flowing nitrogen gas. An initial ramp was used to reach 400 °C in 90 min, and a second ramp was applied to reach 750 °C in 120 min. The sample was maintained at 750 °C for 2 h. Samples were then cooled to ambient conditions and removed from the oven. The as-synthesized carbon materials were denoted as Activated Hydrochar_X_Y, where X and Y represented the HTC temperature (°C) and HTC residence time (h), respectively. For comparison, raw CCR was also placed in a quartz boat within the tubular furnace and directly pyrolyzed using the same heating ramps, and the resulting carbon material was denoted as pyrochar.

Characterization Methods

The elemental analysis (C, H, N, and S) was performed using a Vario MICRO cube analyzer (Elementar, Germany), and the oxygen content was calculated by the balance. Fourier transform infrared (FTIR) spectra of the materials in powder form were recorded from 400 to 4000 cm^{-1} at a resolution of 4 cm^{-1} using a Bruker Vertex 70 FTIR spectrometer (Bruker, Germany) with the KBr disc method. The activated hydrochars and pyrochar were determined by the N_2 adsorption-desorption isotherms at -196 °C using Autosorb-iQ (Quantachrome Instruments, Boynton Beach, FL, USA). Prior to adsorption analysis, the samples were outgassed at 300 °C for 6 h. The specific surface areas were evaluated using the Brunauer-Emmett-Teller (BET) method.

Adsorption Experiments

The batch adsorption experiments were conducted at 30 °C using a temperature-controlled shaker. Prior to adsorption, the adsorbents were dried at 100 °C overnight, and 100 to 1000 mg/L phenol and PNP solutions were prepared using deionized water. Approximately 0.02 g adsorbents were mixed with 15 mL of solutions containing different concentrations of phenol or PNP in a set of 20-mL vials. To ensure sufficient mixing, the vials were placed horizontally in the shaker and shaken at 200 rpm for 24 h at 30 °C, which was sufficient to reach adsorption equilibrium. The solutions were then passed through a syringe filter (PTFE, hydrophilic, 0.25 μm).

The solute concentrations were analyzed by a Waters e2695 high-performance liquid chromatography (HPLC) apparatus (Milford, MA, USA) equipped with a Waters 2489 UV-Vis detector and an ODS-C_{18} column. The mobile phase was a methanol/water mixture (60:40, v/v), and the flow rate was 1.0 mL/min. The column was maintained at 50 °C, and phenol and PNP were detected at 270 nm. The amount adsorbed was calculated by the material balance:

$$q_e = \frac{V(C_0 - C_e)}{m} \tag{2}$$

where q_e is the amount adsorbed (mg/g) at equilibrium, V is the volume of the liquid solution (L), C_0 and C_e are the initial and equilibrium solute concentrations (mg/L), and m is the mass of adsorbent (g).

RESULTS AND DISCUSSION

Yield of Hydrochars

The CCR was submerged in water to ensure that the hydrothermal reaction occurred during the whole reaction process. A maximum of 10 g CCR was loaded when 40 mL of water was charged in the PPL cup; solid/liquid mass ratios of 1:4 and 1:8 were applied. HTC of CCR was carried out in hot compressed water at two different temperatures of 220 and 250 °C, and the residence times were set to 2, 4, and 6 h. The yields of hydrochars generated at different HTC conditions are compared with the yield of pyrochar in Fig. 1. As expected, product yields were higher in the hydrochars (26.7 to 45.2 wt%) than in the pyrochar (22 wt%). With increasing residence time from 2 to 6 h, when the solid/liquid ratio was 1:4, the hydrochar yield decreased from 45.2 to 35.9% at 220 °C, and from 34.8 to 31.8% at 250 °C. The influence of the residence time on yield at both temperatures and solid/liquid ratios was similar, and prolonged residence time led to a decreased yield. Meanwhile, the yields of hydrochars at 250 °C at the same residence time were lower than those of hydrochars at 220 °C. The higher solid/liquid ratio led to a higher yield of hydrochar; a small but noticeable decrease in mass recovery was observed when the solid/liquid ratio was decreased from 1:4 to 1:8. Based on these results, the CCR/water weight ratio of 1:4 was used for subsequent experiments.

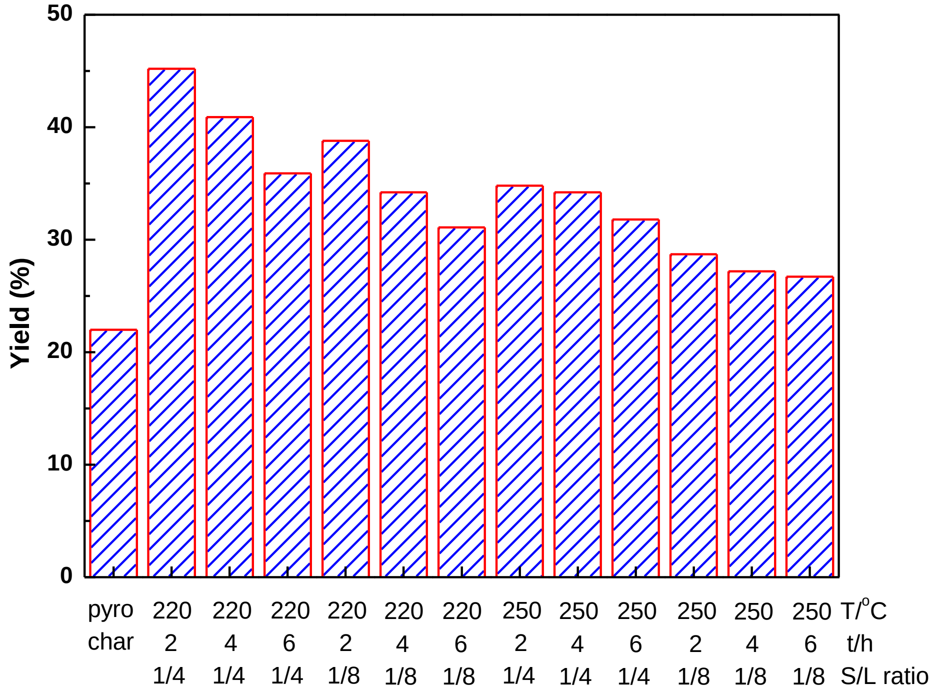

Fig. 1. Solid mass yield of the pyrochar and hydrochars prepared in different HTC conditions

Adsorption Properties of Hydrochars

Preliminary adsorption tests were performed to evaluate the removal of phenol and PNP by the hydrochars and pyrochar; the adsorption isotherms are presented in Fig. 2. The adsorption capacities for both phenols followed the order of Pyrochar > Hydrochar_250_2_1/4 > Hydrochar_220_2_1/4. Hydrochar generated at 250 °C had higher adsorption than its counterpart at 220 °C, suggesting that the more carbonized hydrochar exhibits higher adsorption. However, both hydrochars exhibited lower adsorption capacities than the pyrochar, especially for phenol. Therefore, hydrochars prepared from CCR need further activation to increase their adsorption.

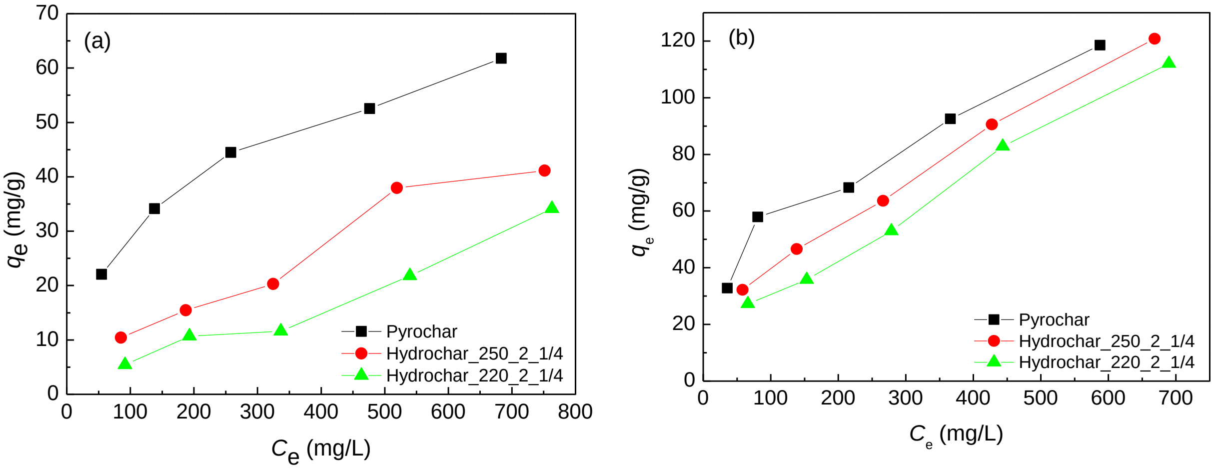

Fig. 2. The adsorption capacities of (a) phenol and (b) PNP on hydrochars and pyrochar from water at 30 °C

Adsorption Properties of Activated Hydrochars

KOH and phosphoric acid are known to be very effective activating agents for carbon materials, but it is environmentally harmful to use large amounts of caustic agents (Falco *et al*. 2013*a*; Qi *et al*. 2014). In this work, thermal activation under N_2 atmosphere, an environment-benign method, was used to enhance the porosity and adsorption performance of HTC hydrochars. The temperature of physical activation is usually in the range of 750 to 900 °C (González *et al*. 2006). In order to avoid excessive degradation of the organic substrate and to retain some of the oxygen-containing functional groups, 750 °C was applied in this work. To understand the effect of the HTC residence time on the adsorption properties, hydrochars prepared at 2, 4, and 6 h were activated and used for the adsorption of phenol and PNP from water (Fig. 3). The adsorption capacities of phenol and PNP on Activated Hydrochar_220_2 were exceptional: superior to pyrochar, and greatly exceeding those of other activated hydrochars. Activated Hydrochar_220_6 and Activated Hydrochar_250_6 had almost identical adsorption capacities for phenol and PNP, which implied that for activated hydrochars, hydrothermal pretreatment temperature at 220 or 250 °C has little effect. Hydrochars obtained at longer residence times of 4 and 6 h adsorbed considerably less phenols than that obtained at 2 h. Prolonged HTC residence time showed a negative effect. It is unexpected that hydrochars with higher degrees of carbonization adsorbed less phenol and PNP after thermal activation than the pyrochar.

The further activation of Hydrochar_220_2 *via* thermal pyrolysis under an inert N_2 atmosphere increased the adsorption of phenol and PNP from water. As shown in Fig. 3, there was a 4 to 5-fold improvement in adsorption compared with the directly pyrolyzed CCR (calcination alone). Because Hydrochar_220_2 was preferable as a precursor for conversion to functional carbon material, this material is a good candidate for an adsorbent to remove phenols from water streams.

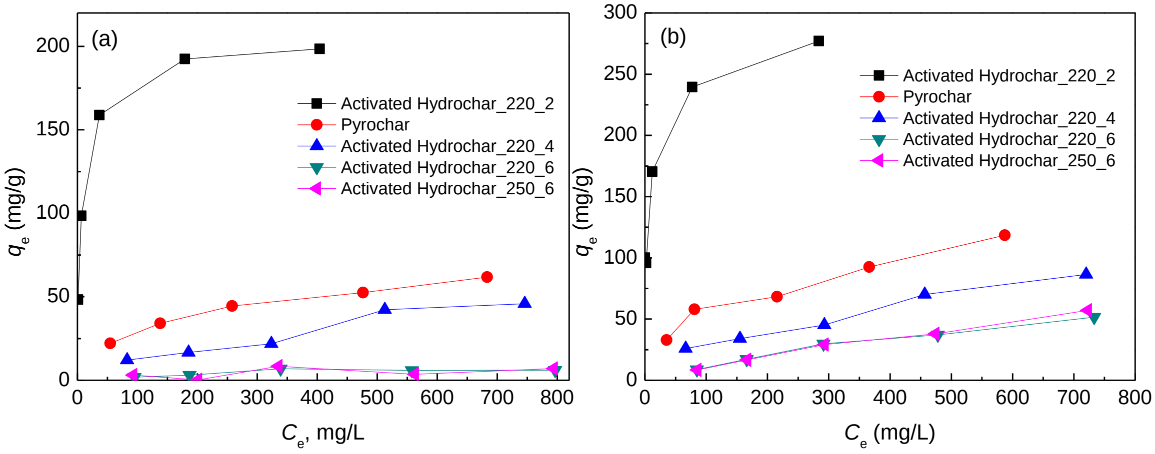

Fig. 3. The adsorption capacities of (a) phenol and (b) PNP on activated hydrochars and pyrochar from water at 30 °C

Materials Characterization

The adsorption properties of different hydrochars, activated hydrochars and pyrochar were quite different. To understand the experimental observations, adsorbents were characterized by the elemental analysis, FTIR, and N_2 adsorption/desorption.

The elemental compositions of different adsorbents are present in Table 1. As expected, pyrochar has higher C content and lower O content than the hydrochars. Further thermal activation of the hydrochars increased the C content to a higher value than the pyrochar and decreased the O content to a lower value than the pyrochar. It is interesting to note that all the four activated hydrochars exhibit similar elemental compositions.

The primary differences in the FTIR spectra for the pyrochar, hydrochars, and activated hydrochars in the wavenumber range of 4000 to 400 cm^{-1} are shown in Fig. 4. The main identified peaks include –OH, aromatic C=O, aromatic C=C, and C–O. The types of functional groups are normally the same, but the number of functional groups are different when considering the different elemental compositions. The hydrochars have higher C=O, C–O, and –OH oxygen-containing functional groups than the pyrochar.

Table 1. Elemental Analysis of Pyrochar and Hydrochars Prepared from Corncob Residues

Adsorbent	C (%)	H (%)	O (%)^a	N (%)	S (%)
Pyrochar	76.05	1.72	21.33	0.47	0.432
Hydrochar_220_2_1/4	54.23	5.26	40.14	0.32	0.051
Hydrochar_250_2_1/4	67.36	4.44	27.74	0.42	0.038
Activated Hydrochar_220_2	87.08	1.32	10.78	0.68	0.139
Activated Hydrochar_220_4	85.46	1.26	12.74	0.50	0.043
Activated Hydrochar_220_6	86.50	1.04	11.67	0.68	0.107
Activated Hydrochar_250_6	85.08	1.03	12.97	0.78	0.144
^{a} Balanced					

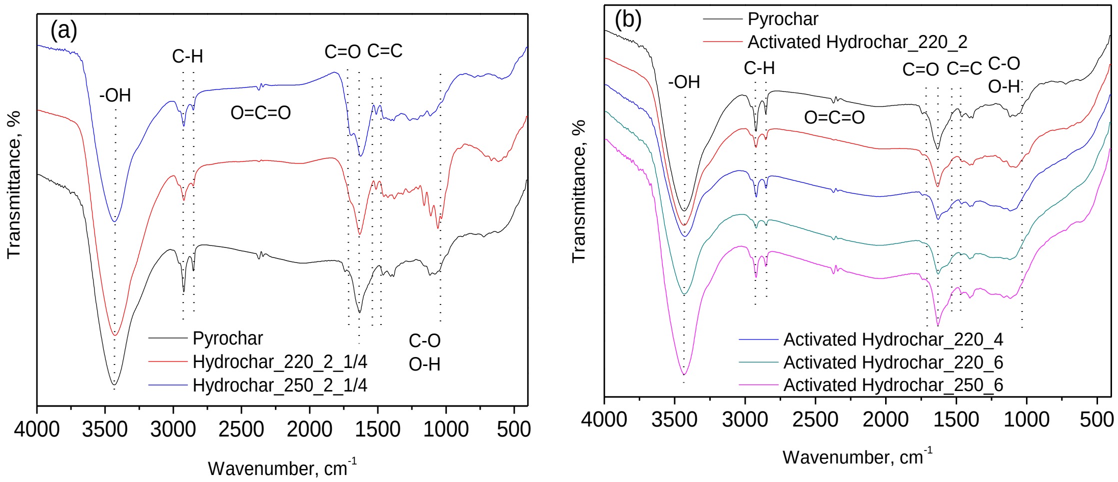

Fig. 4. FTIR spectra of (a) pyrochar and hydrochars (b) activated hydrochars and pyrochar

The N_2 adsorption/desorption isotherms of pyrochar and several activated hydrochars at -196 °C are shown in Fig. 5. The specific surface areas, pore volumes, and average pore diameters of the samples are summarized in Table 2. When CCR was pyrolyzed directly at 750 °C without previous hydrothermal treatment, the pyrochar exhibited a moderate porosity with a BET surface area of 481 m^2/g and a total pore volume of 0.273 cm^3/g.

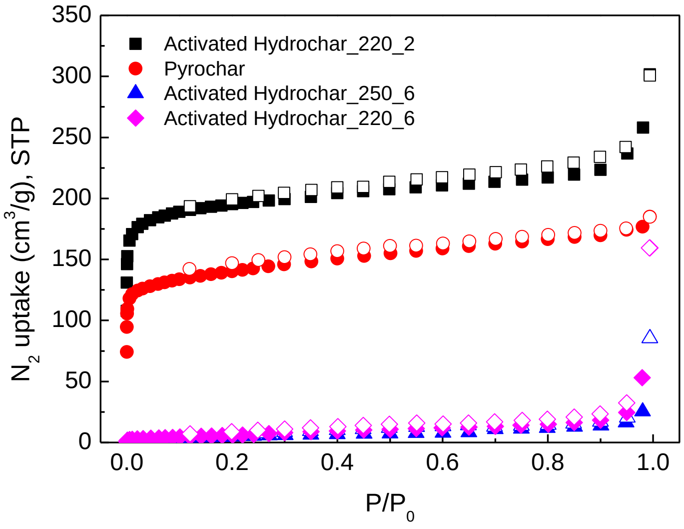

Fig. 5. Nitrogen adsorption (solid) and desorption (open) isotherms at –196 °C for activated hydrochars and pyrochar

Hydrochars produced *via* HTC usually have small pore volumes and low surface areas (< 50 m^2/g) (Sevilla and Fuertes 2009a,b; Román *et al*. 2013). Lignocellulosic biomass-derived HTC hydrochars are good precursors for the preparation of porous carbonaceous materials *via* physical activation of calcination under inert atmosphere. For the hydrochar prepared at 220 °C and 2 h residence time, the post-synthesis carbonization at moderate temperature (750 °C) further increased the surface area and pore volume to 666.7 m^2/g and 0.399 cm^3/g, respectively. However, the N_2 adsorption/desorption measurements revealed that both hydrochars prepared at 220 and 250 °C under 6 h residence time had very low porosities even after thermal activation, with BET surface areas of less than 25 m^2/g. According to the IUPAC classification (Rouquerol *et al*. 1994), Activated Hydrochar_220_2 and pyrochar showed Type I isotherm behavior, which is characteristic of microporous materials. The other two activated hydrochars showed typical Type II isotherm behavior and were non-porous materials, which may explain their low adsorption performance for both phenols. Compared with pyrochar, Activated Hydrochar_220_2 exhibited improved porosity and dramatically higher adsorption capacities for phenol and PNP. Therefore, hydrochar prepared at 2 h has a higher tendency to develop micropores during thermal activation than hydrochars prepared at a longer residence time. Therefore, the exceptional adsorption properties of Activated Hydrochar_220_2 for phenols may be attributed to the combination of porosity and surface groups.

Table 2. Physical Properties of Activated Hydrochars and Pyrochar Prepared from Corncob Residues

Adsorbent	S_{BET} [a] (m^2/g)	V_{tot} [b] (cm^3/g)	V_{micro} [c] (cm^3/g)	Average Pore Diameter (nm)
Activated Hydrochar_220_2	666.7	0.399	0.321	1.93
Pyrochar	480.8	0.273	0.240	2.01
Activated Hydrochar_220_6	23.3	0.082	0.017	40.4
Activated Hydrochar_250_6	17.5	0.039	0.011	30.2

[a] BET specific surface area was calculated in the P/P_0 range of 0.06-0.18
[b] Total pore volume was calculated by taking the data at P/P_0 = 0.98
[c] Micro pore volume was calculated by taking the data at P/P_0 = 0.5

Adsorption Isotherms

The most commonly used Langmuir, Freundlich, and Sips isotherm models were tested to correlate the experimental equilibrium data of phenol and PNP on the best performance material, Activated Hydrochar_220_2. The Freundlich model is given by Eq. 3. The Sips and Langmuir (n = 1) models take the same form as Eq. 4,

$$q_e = K_f C_e^{1/n_\mathrm{f}} \tag{3}$$

$$q_e = \frac{q_\mathrm{m} b C_\mathrm{e}^n}{1 + b C_\mathrm{e}^n} \tag{4}$$

where K_f is an indication of the adsorbent capacity, $1/n_\mathrm{f}$ is a measure of the surface heterogeneity, ranging between 0 and 1; q_m is the maximum adsorption capacity (mg/g), b is the adsorption equilibrium constant (L/mg), and n is the Sips parameter.

The best-fit curves are shown in Fig. 6, and the resulting parameter values are presented in Table 3. It is evident that both the Langmuir and Freundlich models failed to correlate the adsorption isotherms of both phenols, resulting in considerable deviation. The adsorption isotherms of both phenols were correlated by the three-parameter Sips equation with excellent fits ($R^2 > 0.999$). The adsorption capacities were tremendous, with q_m values for phenol and PNP up to 216.3 and 326.8 mg/g, respectively.

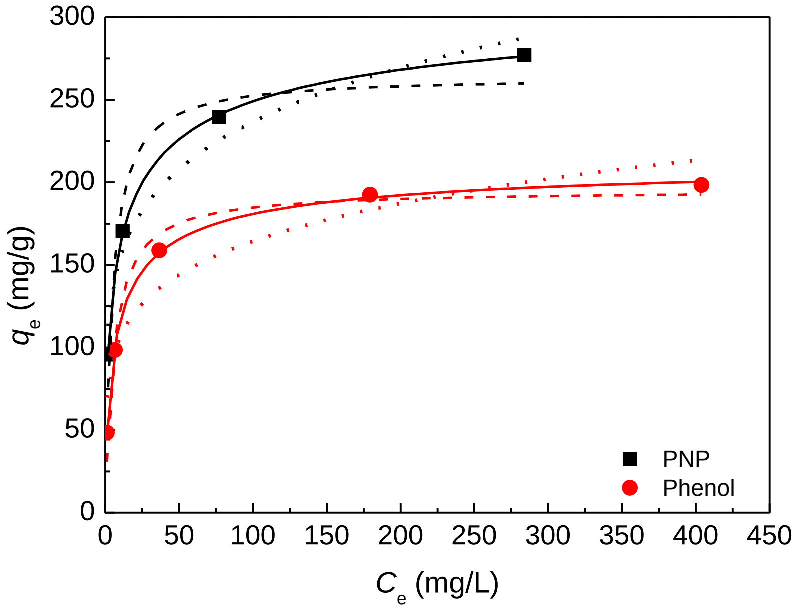

Fig. 6. Adsorption isotherms of phenol and PNP on Activated Hydrochar_220_2 showing the experimental data and fitting by different isotherm models. The dotted, dashed, and solid lines are the Freundlich, Langmuir, and Sips models, respectively.

Table 3. Fitting of Various Adsorption Isotherms for the Adsorption of Phenol and PNP on Activated Hydrochar_220_2

	Langmuir			Freundlich			Sips			
	q_m (mg/g)	*b* (L/mg)	R^2	K_f	$1/n_f$	R^2	q_m (mg/g)	*b* (L/mg)	*n*	R^2
Phenol	195.4	0.174	0.971	68.95	0.188	0.922	216.3	0.262	0.645	0.999
PNP	264.3	212.1	0.941	363.4	0.186	0.962	326.8	10.45	0.514	0.999

The comparison of the adsorption capacities of phenol and PNP on the best performance material of this work with some alternative adsorbents reported in the literature are summarized in Tables 4 and 5, respectively. It is not easy to compare the adsorption performance of different adsorbents because the experimental conditions (especially the concentration range) were usually different. Here the amounts adsorbed at equilibrium concentration of 100 mg/L (or 100 mg/g adsorbed for phenol) and the maximum adsorption capacities of various adsorbents were selected for comparison. Activated Hydrochar_220_2 exhibited exceptional adsorption capacities for phenol and PNP, far exceeding most other adsorbents.

The maximum adsorption capacities of HPR, CC-1.6, RH-1.6, and NDA-701 were higher than those of Activated Hydrochar_220_2, which is attributed to the higher concentration ranges applied in the liquid phase. Activated Hydrochar_220_2 was superior or equal to the best-performing activated carbons (Filtrasorb 400 and AQ40) and only slightly lower than the activated carbon fiber. Therefore, the conjunction HTC and thermal activation processes are a promising approach to upgrade CCR to a high-quality carbon material under mild conditions.

Table 4. Comparison of the Adsorption Capacities of Phenol from Water on Various Adsorbents

Adsorbent	T (°C)	Adsorption capacity		q_{max} (mg/g)	Reference
		C_e (mg/L)	q_e (mg/g)		
NH_2-MIL-101(Al)	30	100	5	NA	Liu *et al*. 2014
Carbon nanospheres (CNS) by the direct pyrolysis of benzene	NA	100	13	NA	Lazo-Cannata *et al.* 2011
Chemically modified chitosan	30	100	25	132	Li *et al.* 2009
Hyper-cross-linked polyphosphamide resin, HPR		~1800	100	516 [a]	Zeng *et al*. 2011
Amberlite XAD-4	25	100	53	196	Păcurariu *et al.* 2013
PS_DVB functionalized with carboxylic acid groups	25	100	99	208	Păcurariu *et al.* 2013
N-methylacetamide-modified hypercrosslinked resin, HJ-Z01	25	100 150	76 100	236	Huang *et al*. 2012
Hypercrosslinked polymeric adsorbent, NJ-8	30	100 170	78 100	NA	Li *et al.* 2002
Commercial activated carbon	30	50	100	166	Kumar *et al.* 2007
Activated carbon derived from rattan sawdust	30	20 100	115 140	149	Hameed and Rahman 2008
CC-1.6 (pyrolyzed corncobs)	40	~1600	100	296 [b]	Liu *et al*. 2011
RH-1.6 (pyrolyzed rice-husks)	40	~1300	100	589 [b]	Liu *et al*. 2011
Commercial activated carbon F400	25	100	122	160	Álvarez *et al*. 2005
Commercial activated carbon AQ40	25	100	141	189	Álvarez *et al*. 2005
Activated Hydrochar_220_2	30	20 100	100 175	216	This work

NA: not available
PS-DVB: Poly(styrene-co-divinylbenzene)
[a] Phenol concentration up to 9000 mg/L
[b] Phenol concentration up to 15000 mg/L

CONCLUSIONS

1. Corncob residue (CCR) hydrochar prepared by hydrothermal carbonization (HTC) at 220 °C and 2 h was further activated at 750 °C using thermal pyrolysis under N_2 atmosphere to fabricate a porous carbon material. This material exhibited very promising performance towards the adsorption of phenol and *p*-nitrophenol (PNP) from water, with 4- to 5-fold improvement of the adsorption capacity compared with the directly pyrolyzed CCR (calcination alone).
2. The effect of the HTC conditions on hydrochar yields was examined at two different temperatures (220 and 250 °C), three residence times (2, 4, and 6 h), and two CCR/water weight ratios (1:4 and 1:8). With increasing temperature and time, the HTC hydrochar yield decreased. A higher solid/liquid ratio resulted in higher HTC hydrochar yield. The hydrochars exhibited lower adsorption performance than the directly pyrolyzed CCR.

3. The HTC residence time was extremely important in the porosity development and adsorption properties. HTC hydrochars with higher degree of carbonization (4 and 6 h residence time) could not be further upgraded to functional carbon materials *via* thermal activation.
4. This paper illustrates that HTC hydrochars of lignocellulosic biomass are good precursors to produce carbon materials with particular application for water purification. The conjunction of HTC and thermal activation processes is a promising way to convert CCR to high-quality carbon materials under mild conditions.

Table 5. Comparison of the Adsorption Capacities of PNP from Water on Various Adsorbents

Adsorbent	T (°C)	Adsorption capacity		q_{max} (mg/g)	Reference
		C_e (mg/L)	q_e (mg/g)		
Fly ash	30	100	4.8	9.91	Sarkar and Acharya 2006
Chemically modified chitosan	30	100	10	44.9	Li *et al.* 2009
Carbon nanospheres (CNS) by the direct pyrolysis of benzene	NA	100	18	NA	Lazo-Cannata *et al.* 2011
H_3PO_4-treated coal	NA	100	60	256	Ahmaruzzaman and Sharma 2005
Hypercrosslinked resin HJ-1	32	100	139	190	Huang et al. 2009
NH_2-MIL-101(Al)	30	100	167	193	Liu *et al.* 2014
Amberlite XAD-4	30	100 200	59.2 84	NA	Li *et al.* 2002
Hypercrosslinked polymeric adsorbent, NJ-8	30	100 200	180 231	NA	Li *et al.* 2002
Hypercrosslinked resin NDA-701	30	100	190	385 [a]	Pan *et al.* 2007
Commercial activated carbon	30	100	220	333 [a]	Pan *et al.* 2007
Commercial activated carbon	30	100 200	180 200	206	Kumar *et al.* 2007
Commercial activated carbon F400	25	100	180	245	Álvarez *et al*. 2005
Commercial activated carbon AQ40	25	100	280	329	Álvarez *et al*. 2005
Activated carbon fiber	35	100	305	370	Tang *et al.* 2007
Activated Hydrochar_220_2	30	100 200	250 270	327	This work

NA: not available
[a] PNP concentration up to 2200 mg/L

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