Use of Starbon for the Adsorption and Desorption of Phenols

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ABSTRACT: Novel materials, Starbon, prepared from naturally abundant polysaccharides, such as starch and alginic acid, have demonstrated significant potential as adsorbents for the uptake of a range of phenolic compounds. The experimental results revealed that the materials exhibited high efficiency to remove phenols from aqueous media due to their high mesoporous nature. The adsorption process was described well by the Langmuir and Freundlich isotherms. Thermodynamic analysis of the results indicated that adsorption was a physical process and is in agreement with data obtained from the Dubinin−Radushkevich isotherm model. Enthalpy of adsorption varied from endothermic to exothermic for different adsorbents and phenolics. Regeneration of Starbon was attempted using a range of pH with phenol recovery of up to 40% achieved. This work demonstrates the effectiveness of a green sustainable adsorbent for removal of hazardous compounds from aqueous waste streams.

KEYWORDS: Adsorption isotherms, Phenol, Porous materials, Polysaccharide, Thermodynamics

INTRODUCTION

Phenolic compounds are released into the environment as part of many industrial effluents, including petroleum refineries, steel foundries, and herbicide industries.[1] They are potentially toxic and carcinogenic, posing significant threat to the biosphere. Therefore, it is imperative that they are removed from wastes for safe disposal. Liquid-phase adsorption processes have been shown to be highly efficient for the removal of pollutants from aqueous waste streams.[2,3]

Polysaccharides are abundant, renewable, and biodegradable resources that are capable of associating with a wide variety of molecules due to a range of physical and chemical interactions.[4−7] It has been reported that polysaccharides such as starch and alginic acid can be utilized to generate porous materials, known as Starbon, using a method of expansion, retrogradation, and controlled pyrolysis.[8−10] This method of preparation utilizes the inherent ability of these natural polymers to organize into nanoscale lamellar structures. The process results in materials with 80−90% mesoporosity without the use of templating agents or highly aggressive chemicals that are typically necessary. A range of surface functionalities, from oxygen rich at low temperatures to highly aromatized above 700 °C, can also be obtained through variation in preparation temperature of the materials (Figure 1). Previous work has already shown that Starbon are efficient adsorbers of large organic molecules such as dyes; however, their affinity to adsorb small organic molecules has not before been investigated.

Herein, we present the feasibility of two Starbon adsorbents derived from two different polysaccharides and prepared at 800 °C, starch derived (S800) and alginic acid derived (A800), for removal of a range of phenolics from aqueous solutions. The affect of differing polysaccharide type on adsorption capacity is
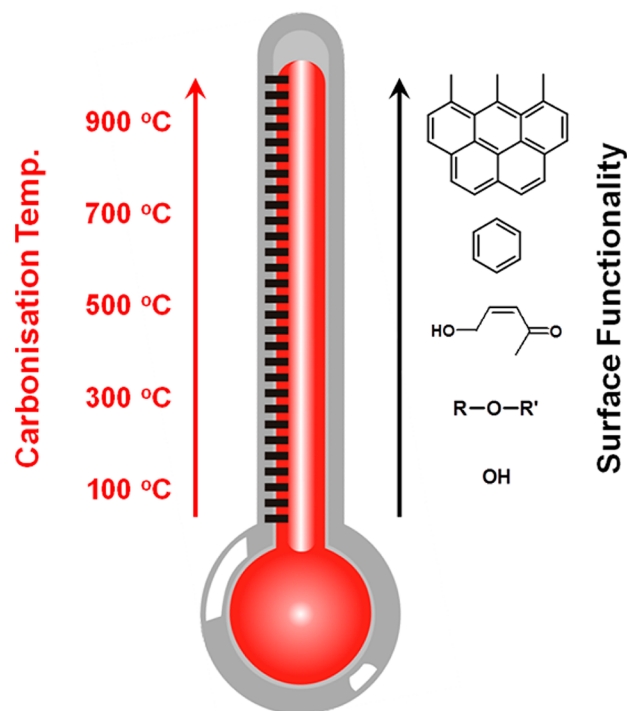

Figure 1. Development of the surface functionality of Starbon upon pyrolysis.

investigated. Isotherm models (Langmuir, Freundlich, and Dubinin–Radushkevich) were used to determine the mechanism of adsorption for these materials. Initial results of nondestructive regeneration of Starbon by desorption are also presented as a potential method for not only recovery of the adsorbent but also recovery of the phenolic compound for further use.

■ EXPERIMENTAL SECTION

Materials. All materials were used as received without further purification. Phenol (P), *o*-cresol (OC), 2-fluorophenol (2F), 3-aminophenol (3A), 4-methoxyphenol (4M), alginic acid, and all solvents were all purchased from Sigma-Aldrich. Unmodified corn starch was purchased from National Starch. Preprepared solutions of sodium hydroxide (1 mol) and hydrochloric acid (0.1 mol) used in pH desorption were purchased from Fisher Scientific.

Preparation of Starch-Derived Starbon S800. Corn starch (1.6 kg) was added to 8 L of deionized water and heated at 120 °C/80 kPa for 45 min. The resulting gel was retrograded at 5 °C for 48 h. The gel was subject to five solvent exchanges with ethanol. The filtered material was then oven dried to yield expanded starch. This was doped with *p*-toluenesulfonic acid (5% w/w) and refluxed for 6 h. The resulting material was heated at 1 °C min^{-1} in an inert atmosphere to 800 °C. This material is referred to as S800.

Preparation of Alginic Acid-Derived Starbon A800. Alginic acid (40 g) was added to 800 mL of deionized water and heated at 90 °C for 2 h. The gel was retrograded for 12 h at 5 °C. The gel was subjected to five solvent exchanges with ethanol and dried using supercritical CO_2 at 40 °C, 100 bar, and 40 g min^{-1} for 3 h. The resulting material was heated at 1 °C min^{-1} in an inert atmosphere to the required temperature 800 °C. This material is referred to as A800.

Adsorption Experiments. To determine the adsorption capacity of the materials, batch experiments were employed. Adsorption isotherms were recorded over a concentration range of 25–200 mg L^{-1} of phenolic solution at 298 K. For the experiments, 20 mL of solution and 20 mg of adsorbent were stirred, and samples were taken at 24 h. The adsorption capacity of the materials (qe) was determined by

$$q_e = (C_0 - C_e)\frac{V}{m} \tag{1}$$

where C_0 is the initial concentration of the solution, C_e the concentration of the sample solution, V the volume of solution used (L), and m the mass of adsorbent used (g). A Jasco V-550 UV–vis spectrometer was used to determine the extent of phenolic removal. Compounds were identified using max wavelengths: P λ = 270, OC λ = 270, 2F λ = 267, 3A λ = 282, and 4 M λ = 288.

pH Desorption Experiments. To determine if the phenolic compound can be desorbed from the adsorbent, first adsorption experiments were carried out for 24 h. Samples were taken to determine the amount adsorbed. pH of the experiments were then altered using NaOH and HCl and allowed to desorb for 24 h and sampled again.

■ RESULTS AND DISCUSSION

Characterization of Starbon. The fundamental functional and textural properties of the materials are displayed in Table 1.

Table 1. Characteristics of Starbon S800 and A800

	surface area^a (m^2 g^{-1})	pore volume^a (cm^3 g^{-1})	micropore volume^a (cm^3 g^{-1})	degree of aromatization^b (%)
S800	535	0.75	0.22	28
A800	265	1.08	0.04	45

^{a}Data obtained using N2 porosimetry. ^{b}Data obtained from XPS analysis.

The results show some variation in the materials that arises from the differing polysaccharide starting materials; the starch-derived material (S800) exhibits more than double the surface area compared to the alginic acid-derived material (A800), which may allow for higher adsorption capacities. Interestingly S800 has a lower pore volume with more of the volume contributed by micropores, which may be detrimental to uptake ability. XPS analysis revealed that A800 exhibited a considerably larger degree of surface aromatization than S800, likely caused by a difference in starting material, and may offer an advantage to the adsorption of phenols. (For a more thorough characterization of these materials please see ref 10).

Effect of Initial Phenolic Concentration on Adsorption Capacity. Effect of initial phenolic concentration on adsorption was investigated at concentrations ranging from 25 to 200 mg L^{-1} at 298 K (Figure 2). Overall, for all
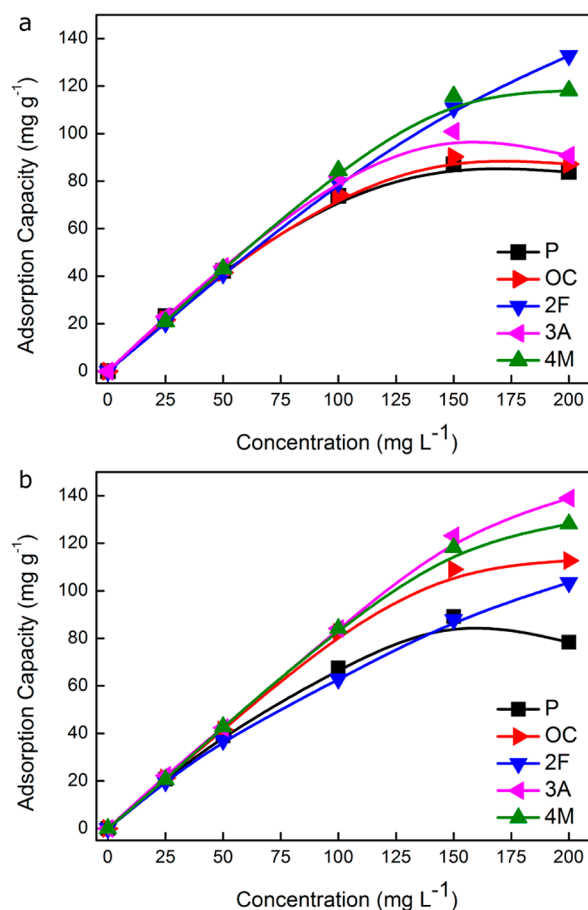

Figure 2. Equilibrium adsorption capacities obtained at different initial phenolic concentrations by (a) S800 and (b) A800.

adsorbents and phenols, the adsorption capacity increased with an increase in phenolic concentration due to improved interaction between the phenolic and Starbon at higher concentrations. A800 showed higher adsorption capacities overall, which is supported by previous work using Starbon where it was shown that this is a result of the increased mesoporous nature and larger pore diameters of A800 in comparison to S800, allowing more of the available adsorptions capacity to be utilized through pore filling.[10] Comparison of Starbon adsorption capacities with a range of other adsorbents are listed in Table 2, encouragingly, S800 and A800 show

Table 2. Adsorption Capacities of Starbon Compared with Other Adsorbents

adsorbent	surface area (m²/g)	phenol	temperature (K)	adsorption capacity (mg/g)	reference
S800	535	phenol	298	87	current work
		o-Cresol		90	
		2-fluorophenol		133	
		3-aminophenol		101	
		4-methoxphenol		118	
A800	265	phenol	298	89	current work
		o-Cresol		113	
		2-fluorophenol		104	
		3-aminophenol		139	
		4-methoxphenol		128	
coir pith carbon	167	2-chlorophenol	308	18	19
rice husk	439	m-cresol	298	22	20
apricot stone shells	1306	phenol	unknown	120	21
50% H3PO4 500 °C		m-cresol		101	
		p-cresol		108	
		2-chlorophenol		120	
coconut coir pith	470	phenol	303	37	22
coconut shell	1062	p-chlorophenol	294	334	11
wood; pica	1699			309	
coal; SP	865			231	
straw	322			129	
tire	346			206	

comparable or superior adsorption to many of these other materials. The coconut shell, wood, coal, and tire do demonstrate higher adsorption capacities; however, it should be noted that these materials contain a significantly greater surface area.[11] A large proportion of this surface area was contributed by narrow mesopores and micropores; it is well known that such porous systems lead to limited desorption due to high surface energy of these pores.[7]

Other examples of adsorption with activated carbons not shown in the table include those derived from bagasse and wood charcoal. These have previously shown promise in phenol adsorption studies.[12]

Adsorption Isotherms. In order to investigate the mechanism of P, OC, 2F, 3A, and 4 M adsorption on the Starbon materials, the experimental data were applied to the Langmuir, Freundlich, and Dubinin−Radushkevich isotherm equations (Figure 3). The constant parameters of the isotherm equations for this adsorption process were calculated by regression using a linear form of the isotherm equations. The constant parameters and correlation coefficient (R^2) are summarized in Tables 3 and 4.

Langmuir Isotherm. The Langmuir adsorption isotherm for monolayer adsorption on a homogeneous surface has been successfully applied to many adsorption processes.[13] The linear form of the equation was used for this work

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \tag{2}$$

$$Q_0 = \frac{K_L}{a_L} \tag{3}$$

where Ce is the dye concentration at equilibrium (mg/L), qe is the adsorption capacity at equilibrium, and a_L and K_L are Langmuir adsorption constants. Q_0 is the monolayer adsorption capacity of the solid (mg/g).

Freundlich Isotherm. The Freundlich equation is employed to describe heterogeneous systems in which it is

characterized by the heterogeneity factor $1/n$. The linear form of the equation is used for this work

$$\ln q_e = \ln kf + \frac{1}{n} \ln C_e \tag{4}$$

where kf is the Freundlich constant (L/g) and is linked to adsorbence capacity of the solid. $1/n$ is the heterogeneity factor and signifies the intensity of adsorption. A n of greater than unity indicates favorable adsorption of the adsorbate molecule.[14] The Freundlich equation predicts that the phenolic concentrations on the adsorbent will increase as long as the concentration of phenolic increases in the liquid.[15]

Dubinin−Radushkevich (D-R) Isotherm. This equation assumes adsorption is limited to a monolayer and can be used to estimate the energy of adsorption.[16] The linear form of the equation was used to model the adsorption

$$\ln q_e = \ln q_m - K'\varepsilon^2 \tag{5}$$

where ε, the Polanyi potential, is equal to

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{6}$$

where q_m signifies the monolayer saturation capacity (L/g) and K' the constant of adsorption energy, which gives the mean free energy (E) of adsorption per molecule of adsorbate when it is transferred to the surface of the solid from the solution and can be calculated from the following relationship[17]

$$E = \frac{1}{\sqrt{2K'}} \tag{7}$$

The mean adsorption energy (E) gives information about chemical and physical adsorption, where E in the range of 8−16 kJ mol⁻¹ indicates physical adsorption of the adsorbate.[18]

S800 and A800 show good correlation to both the Langmuir and Freundlich isotherms (Tables 3 and 4). From this it can be assumed that first the surfaces of these materials are not
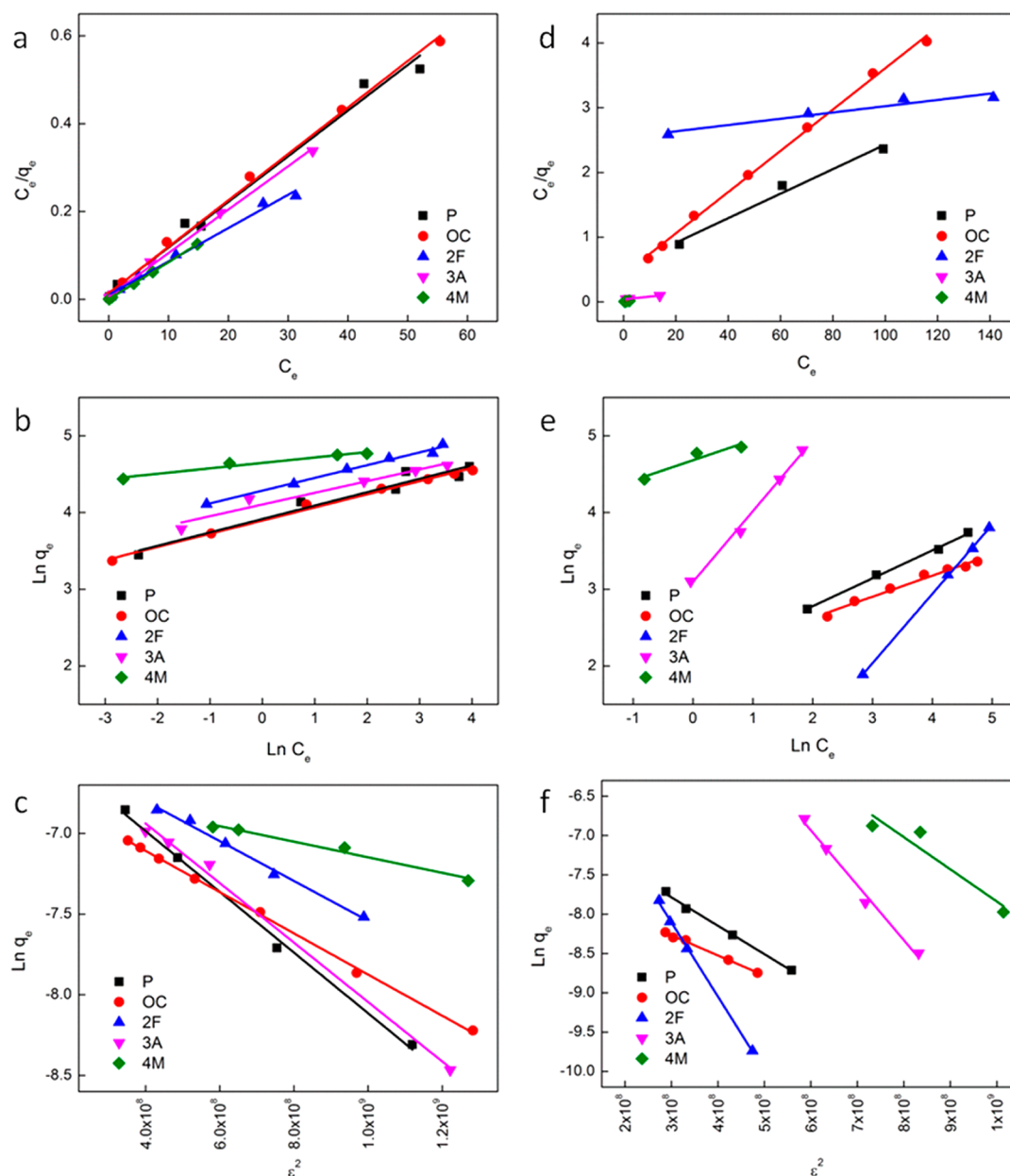
Figure 3. Linearized adsorption isotherms for S800 (a) Langmuir, (b) Freundlich, and (c) D-R, and A800 (d) Langmuir, (e) Freundlich, and (f) D-R.

Table 3. Isotherm Parameters for Phenolic Adsorption on S800

	isotherm parameters	phenol	o-cresol	2-fluorophenol	3-aminophenol	4-methoxyphenol
Langmuir	a_L (L/mg)	1.4 ± 0.6	0.7 ± 0.5	0.7 ± 0.6	1.5 ± 1.3	15.5 ± 1.8
	Q_0 (mg/g)	100.4 ± 1.2	94.6 ± 2.2	131.8 ± 5.9	101.2 ± 2.4	118.6 ± 1.8
	R^2	0.9994	0.9966	0.9899	0.9972	1.0000
Freundlich	kf	50.2 ± 2.9	49.2 ± 0.8	72.6 ± 1.5	60.6 ± 2.7	104.2 ± 5.5
	n	5.7 ± 0.7	5.8 ± 0.2	6.0 ± 0.3	6.6 ± 0.8	14.1 ± 0.3
	R^2	0.9372	0.9924	0.9864	0.9401	0.9503
D-R	q_m x10^{-4} (mol/g)	19.6 ± 1.2	13.6 ± 0.2	18.2 ± 0.7	20.3 ± 1.3	12.7 ± 0.5
	K' × 10^{-9} (mol^2/J^2)	1.9 ± 8.4 x10^{-2}	1.3 ± 1.9 x10^{-2}	1.2 ± 5.8 x10^{-2}	1.8 ± 8.7 x10^{-2}	0.5 ± 4.6 x10^{-2}
	E (kJ/mol)	16.3 ± 0.4	19.8 ± 0.1	20.1 ± 0.5	16.5 ± 0.4	32.2 ± 1.5
	R^2	0.9940	0.9987	0.9952	0.9933	0.9733

homogeneous, a result of residual oxygen functionality leading to heterogeneous energy across the surface. Second, adsorption of the phenolics is going beyond monolayer coverage; this is

not surprising as the mesoporous nature of the adsorbents would easily allow for multilayer adsorption once the monolayer is saturated. The heterogeneity factor (n), calculated

Table 4. Isotherm Parameters for Phenolic Adsorption on A800

	isotherm parameters	phenol	o-cresol	2-fluorophenol	3-aminophenol	4-methoxyphenol
Langmuir	a_L (L/mg)	$8.2 \times 10^{-2} \pm 7.3 \times 10^{-3}$	$7.6 \times 10^{-2} \pm 6.2 \times 10^{-3}$	$1.9 \times 10^{-3} \pm 2.8 \times 10^{-4}$	$0.1 \pm 1.4 \times 10^{-3}$	3.4 ± 0.6
	Q_0 (mg/g)	40.3 ± 7.1	31.4 ± 0.6	206.2 ± 37.7	241.6 ± 15.2	146.0 ± 6.3
	R^2	0.9919	0.9975	0.9113	0.9919	0.9962
Freundlich	kf	7.8 ± 0.3	8.0 ± 0.5	0.5 ± 0.02	22.2 ± 1.3	108.0 ± 5.6
	n	$2.8 \pm 9.1 \times 10^{-2}$	3.6 ± 0.2	$1.1 \pm 1.4 \times 10^{-2}$	$1.1 \pm 5.7 \times 10^{-2}$	3.8 ± 1.3
	R^2	0.9966	0.9754	0.9996	0.9919	0.8339
D-R	q_m x10^{-4} (mol/g)	12.3 ± 0.8	5.5 ± 0.2	51.1 ± 3.4	642.5 ± 215.9	235.6 ± 318.6
	$K' \times 10^{-9}$ (mol^2/J^2)	3.6 ± 0.2	2.6 ± 8.5 x10^{-2}	9.4 ± 0.2	7.0 ± 0.5	4.1 ± 1.3
	E (kJ/mol)	11.8 ± 0.3	14.0 ± 0.2	$7.3 \pm 7.3 \times 10^{-2}$	8.5 ± 0.3	11.1 ± 1.8
	R^2	0.9942	0.9956	0.9988	0.9861	0.8345

from the Freundlich isotherm, is greater than unity for all adsorbates indicating favorable adsorption. The mean adsorption energy (E) shows that the phenolics are favorably physisorbed on to the adsorbent surface.

For S800, the monolayer adsorption capacity, Q_0, calculated from the Langmuir adsorption isotherm, was similar across the range of phenols. This result would suggest that adsorption is relatively unaffected by the nature of the phenol molecule. However, the values of Q_0 for A800 exhibit considerable variation for the different phenolics.

The A800 adsorption capacity increases in the order of OC < P ≪ 4 M < 2F < 3A; this data trend demonstrates a close correlation to the order of electron density on the phenol ring: P > OC > 4 M > 2F > 3A (Table 5). By the addition of electron

Table 5. Charge Distribution of Phenolic Compounds

	electron density[a]	
	phenol ring	phenol oxygen
phenol	−0.508	−0.228
o-cresol	−0.481	−0.226
2-fluorophenol	−0.358	−0.216
3-aminophenol	−0.086	−0.230
4-methoxyphenol	−0.397	−0.227

[a]Calculated using HyperChem.

withdrawing groups, there is less electron density on the phenol ring leading to better uptake, indicative of adsorption through π−π interactions between the adsorbent surface and the adsorbate.[23]

Interestingly, this result indicates a difference in the modes of adsorption occurring for S800 and A800, which is likely to arise from the differences in the material characteristics, such as the higher degree of surface aromatization seen in A800 compared to increased microporosity in S800 affecting the adsorbent/adsorbate interactions. This result could indicate that S800 is a superior material for water purification than A800 as it adsorbs irrespective of phenol characteristics.

Thermodynamic Study of Adsorption. To further understand the adsorption process taking place between Starbon and the adsorbates, thermodynamic parameters were evaluated (Tables 6 and 7). The van't Hoff equation was used to calculate the values of enthalpy (ΔH) and entropy (ΔS)

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{8}$$

where K is the equilibrium constant at temperature T, R is the gas constant (8.314 J mol^{-1} K^{-1}), and T is temperature (K).

The Gibbs free energy was calculated to determine the feasibility of adsorption using the equation

$$\Delta G = RT \ln K \tag{9}$$

For both Starbon materials, the ΔG values for all of the molecules studied were negative across all temperatures inferring that the adsorption is favorable and spontaneous in nature. ΔH and ΔS were calculated from the slope and intercept of the van't Hoff plots. The calculated values of ΔH are all below 40 kJ mol^{-1} indicative of physical adsorption, which is in agreement with the values calculated from the D-R isotherm. For S800 adsorption of OC and A800 adsorption of P, 3A, 4M, the values of enthalpy are positive suggesting endothermic adsorption thus uptake increases with increasing temperature. Adsorption in a solid/liquid system such as the one presented here takes place in two steps: (a) desorption of the molecules of solvent (water) previously adsorbed by the adsorbent and (b) adsorption of the adsorbate. Endothermic adsorption suggests that the adsorbate and adsorbent are not strongly interacting on the surface and that the energy required to first displace the water molecules already adsorbed on the adsorbent is larger than the energy being produced by adsorbent/adsorbate interaction.[24] The value of entropy is also positive in these cases due to increased randomness at the solid/solution interface upon uptake of the phenolics and an increase in the degree of freedom of the adsorbed species.[25]

The adsorption of P, 2F, 3A, and 4 M onto S800 and OC and 2F onto A800 all exhibit negative enthalpy, which corresponds to exothermic adsorption, where uptake will decrease with increasing temperature.[26] The values of entropy are also negative, which shows a decrease in the degrees of freedom of the adsorbed species and suggests strong interactions between the phenolics and Starbon.[27]

It is interesting to note that the thermodynamic values are almost entirely opposite when comparing S800 and A800, as with the isotherm parameters (Section 3.3) this shows that although adsorption capacity for the two materials is similar the mode of adsorption occurring is entirely different.

Desorption of Phenolics. To enable not only reuse of the adsorbent material but also recovery of the adsorbed species, nondestructive desorption techniques were tested; the most effective method observed was the use of pH (Figure 4). Starbon containing phenols were added to aqueous solutions at various pHs ranging from 1 to 14 and analyzed for phenol present in solution after 24 h.

The highest desorption was achieved at pH > 11 for all of the phenolics, which was expected as previous work by Özkaya has shown that sodium hydroxide can react to form a sodium salt of phenol that facilitates desorption.[28] For S800, the amount of

Table 6. Thermodynamic Parameters for Adsorption of Phenolics by S800

adsorbate	S800				
	temperature (K)	ln K	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
phenol	298	0.74	−0.91	−3.8	−9.7
	303	0.90	−0.86		
	308	0.75	−0.82		
	313	0.39	−0.77		
	318	0.29	−0.72		
o-cresol	298	0.65	−1.6	4.2	20
	303	0.66	−1.7		
	308	0.56	−1.8		
	313	0.54	−1.9		
	318	0.74	−2.0		
2-fluorophenol	298	0.94	−2.5	−4.1	−5.4
	303	0.96	−2.5		
	308	0.93	−2.4		
	313	0.92	−2.4		
	318	0.77	−2.4		
3-aminophenol	298	0.22	−0.57	−1.8	−4.0
	303	0.25	−0.55		
	308	0.17	−0.53		
	313	0.10	−0.51		
	318	0.19	−0.49		
4-mMethoxyphenol	298	1.1	−2.8	−4.9	−6.9
	303	1.2	−2.8		
	308	0.92	−2.8		
	313	1.1	−2.7		
	318	0.97	−2.7		

Table 7. Thermodynamic Parameters for Adsorption of Phenolics by A800

adsorbate	A800				
	temperature (K)	ln K	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
phenol	298	0.06	−0.13	1.7	6.0
	303	0.11	−0.16		
	308	0.03	−0.19		
	313	0.07	−0.22		
	318	0.06	−0.25		
o-cresol	298	1.5	−2.8	−16	−43
	303	0.17	−2.6		
	308	0.72	−2.4		
	313	0.64	−2.1		
	318	0.45	−1.9		
2-fluorophenol	298	0.88	−2.0	−11	−32
	303	0.58	−1.8		
	308	0.85	−1.7		
	313	0.46	−1.5		
	318	0.47	−1.4		
3-aminophenol	298	0.21	−0.42	8.9	31
	303	0.11	−0.57		
	308	0.29	−0.73		
	313	0.48	−0.89		
	318	0.30	−1.0		
4-methoxyphenol	298	0.57	−1.2	37	128
	303	0.61	−1.9		
	308	1.0	−2.5		
	313	1.2	−3.1		
	318	0.94	−3.8		

phenolic desorbed was in the order of 2F > P > OC > 3A > 4 M and for A800 was 2F = P > 3A > OC > 4M. Banat et al. observed that desorption was greatly dependent on substituent groups of aromatic compounds; electron-donating groups led to irreversible desorption, while compounds with electron-withdrawing groups showed reversible desorption.[29] The
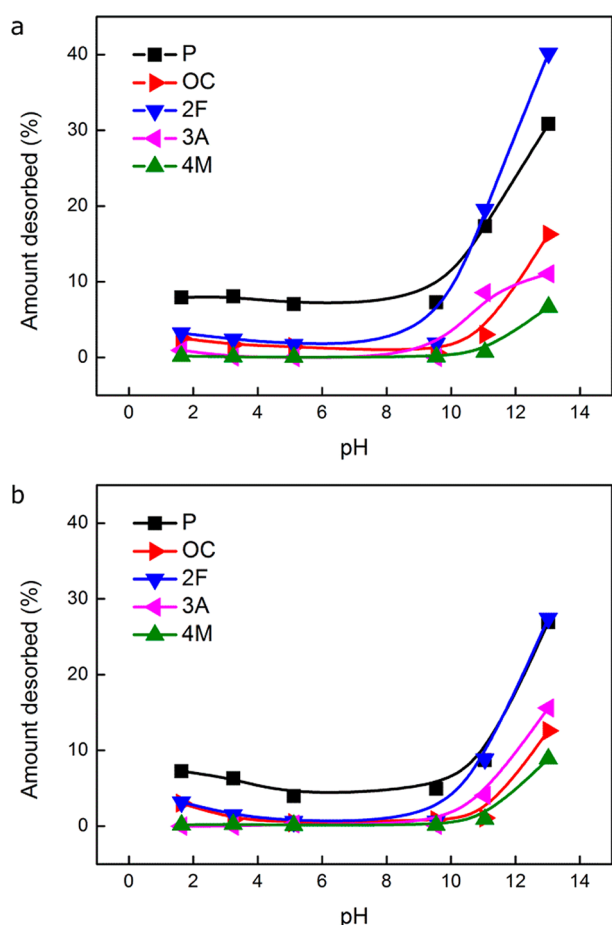
Figure 4. Desorption of phenolics from (a) S800 and (b) A800 by varying pH.

results for Starbon are in good agreement with this hypothesis. Removal of the phenols was between 7−40% was achieved, which is promising for potential recovery of the adsorbate and reuse of the adsorbent; however, an improvement could be achieved by using a flow method of removal rather than batch.

■ CONCLUSIONS

The present work has demonstrated that Starbon are suitable adsorbents for the removal of a range of different phenolic compounds from aqueous waste streams. Adsorption capacities range between 87−139 mg L^{-1}, which is comparable or superior to other biobased adsorbent materials. The Langmuir, Freundlich, and D-R isotherms were all successfully fitted to the data. The fitting revealed that the adsorption was multilayer for both materials, which was expected due to the mesoporous nature of the adsorbents. The mean adsorption energy (E) calculated from the D-R isotherm indicated that all adsorbates were undergoing physical adsorption. Analysis of the isotherm data revealed that adsorption by A800 was greatly dependent on the substituent group on the phenol ring, with monolayer adsorption capacity (Q_0) increasing as the electron-withdrawing effect of the phenol substituent increased. This was not the case for S800, where Q_0 remained relatively similar for all of the adsorbate molecules. These results coupled with the thermodynamic parameters calculated for the two materials indicated that adsorption was occurring by different modes for S800 and A800, which was likely due to the increased microporosity seen in S800 compared to the higher

mesoporosity and degree of surface aromatization for A800. Desorption was achieved between 7−40% by treating the materials with pH > 11 with the highest removal achieved for S800. Further development of the desorption method is required to obtain complete phenol removal and recovery.

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Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) Kumar, A.; Kumar, S.; Kumar, S.; Gupta, D. V. Adsorption of phenol and 4-nitrophenol on granular activated carbon in basal salt medium: Equilibrium and kinetics. *J. Hazard. Mater.* **2007**, *147* (1−2), 155−166.
(2) Moreno-Castilla, C. Adsorption of organic molecules from aqueous solutions on carbon materials. *Carbon* **2004**, *42* (1), 83−94.
(3) Dodson, J. R.; Hunt, A. J.; Parker, H. L.; Yang, Y.; Clark, J. H. Elemental sustainability: Towards the total recovery of scarce metals. *Chem. Eng. Process.* **2012**, *51*, 69−78.
(4) Crini, G. Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Prog. Polym. Sci.* **2005**, *30* (1), 38−70.
(5) Ciesielski, W.; Lii, C.; Yen, M.-T.; Tomasik, P. Interactions of starch with salts of metals from the transition groups. *Carbohydr. Polym.* **2003**, *51* (1), 47−56.
(6) Polaczek, E.; Starzyk, F.; Malenki, K.; Tomasik, P. Inclusion complexes of starches with hydrocarbons. *Carbohydr. Polym.* **2000**, *43* (3), 291−297.
(7) Budarin, V.; Clark, J. H.; Deswarte, F. E. I.; Hardy, J. J. E.; Hunt, A. J.; Kerton, F. M. Delicious not siliceous: Expanded carbohydrates as renewable separation media for column chromatography. *Chem. Commun. (Cambridge)* **2005**, 2903−2905.
(8) Budarin, V.; Clark, J. H.; Hardy, J. J. E.; Luque, R.; Milkowski, K.; Tavener, S. J.; Wilson, A. J. Starbons: New starch-derived mesoporous carbonaceous materials with tunable properties. *Angew. Chem.* **2006**, *118*, 3866−3870.
(9) White, R. J.; Antonio, C.; Budarin, V.; Bergstrom, E.; Thomas-Oates, J.; Clark, J. H. Polysaccharide-derived carbons for polar analyte separations. *Adv. Funct. Mater.* **2010**, *20* (11), 1834−1841.
(10) Parker, H. L.; Hunt, A. J.; Budarin, V.; Shuttleworth, P. S.; Miller, K. L.; Clark, J. H. The importance of being porous: Polysaccharide-derived mesoporous materials for use in dye adsorption. *RSC Adv.* **2012**, *2*, 8992−8997.
(11) Streat, M.; Patrick, J. W.; Camporro Perez, M. J. Sorption of phenol and para-chlorophenol from water using conventional and novel activated carbons. *Water Res.* **1995**, *29* (2), 467−472.
(12) Mukherjee, S.; Kumar, S.; Misra, A. K.; Fan, M. Removal of phenols from water environment by activated carbon, bagasse ash and wood charcoal. *Chem. Eng. J.* **2007**, *129* (1−3), 133−142.
(13) Langmuir, I. The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.* **1918**, *40* (9), 1361−1403.
(14) Basar, C. A. Applicability of the various adsorption models of three des adsorption onto activated carbon prepared waste apricot. *J. Hazard. Mater.* **2006**, *135* (1−3), 232−241.

(15) Wong, Y. C.; Szeto, Y. S.; Cheung, W. H.; McKay, G. Adsorption of acid dyes on chitosan: Equilibrium isotherm analyses. *Process Biochem.* **2004**, *39* (6), 695−704.

(16) Kuleyin, A. Removal of phenol and 4-chlorophenol by sufactant-modified natural zeolite. *J. Hazard. Mater.* **2007**, *144* (1−2), 307−315.

(17) Kim, Y.; Kim, C.; Choi, I.; Rengaraj, S.; Yi, J. Arsenic removal using mesoporous alumina prepared via a templating method. *Environ. Sci. Technol.* **2004**, *38* (3), 924−931.

(18) Benhammou, A.; Yaacoubi, A.; Nibou, L.; Tanouti, B. Adsorption of metal ions onto Morocccan stevensite: Kinetic and isotherm studies. *J. Colloid Interface Sci.* **2005**, *282* (2), 320−326.

(19) Namasivayam, C.; Kavitha, D. Adsorptive removal of 2-chlorophenol by low-cost coir pith carbon. *J. Hazard. Mater.* **2003**, *98* (1−3), 257−274.

(20) Kennedy, L. J.; Vijaya, J. J.; Sekaran, G.; Kayalvizhi, K. Equilibrium, kiinetic and thermodynamic studies on the adsorption of m-cresol onto micro- and mesoporous carbon. *J. Hazard. Mater.* **2007**, *149* (1), 134−143.

(21) Daifullah, A. A. M.; Girgis, B. S. Removal of some substituted phenols by activated carbon obtained from agricultural waste. *Water Res.* **1998**, *32* (4), 1169−1177.

(22) Anirudhan, T. S.; Sreekumari, S. S.; Bringle, C. D. Removal of phenols from water and petroleum industry refinery effluents by activated carbon obtained from coconut coir pith. *Adsorption* **2009**, *15*, 439−451.

(23) Dabrowski, A.; Podkoscielny, P.; Hubicki, Z.; Barczak, M. Adsorption of phenolic compounds by activated carbon - a critical review. *Chemosphere* **2005**, *58*, 1049−1070.

(24) Srivastava, V. C.; Swamy, M. M.; Mall, I. D.; Prasad, B.; Mishra, I. M. Adsorptive removal of phenol by bagasse fly ash and activated carbon: Equilibrium, kinetics and thermodynamics. *Colloids Surf., A* **2006**, *272*, 89−104.

(25) Tang, H.; Zhou, W.; Zhang, L. Adsorption isotherms and kinetics studies of malachite green on chitin hydrogels. *J. Hazard. Mater.* **2012**, *209−210*, 218−225.

(26) Salam, M. A.; Burk, R. C. Thermodynamics and kinetics studies of pentachlorophenol adsorption from aqueous solutions by multi-walled carbon nanotubes. *Water, Air, Soil Pollut.* **2010**, *210*, 101−111.

(27) Khenniche, L.; Benissad-Aissani, F. Adsorptive removal of phenol by coffee residue activated carbon and commercial activated carbon: equilirium, kinetics and thermodynamics. *J. Chem. Eng.* **2010**, *55*, 4677−4686.

(28) Ozkaya, B. Adsorption and desorption of phenol on activated carbon and a comparison of isotherm models. *J. Hazard. Mater.* **2006**, *B129*, 158−163.

(29) Banat, F. A.; Al-Bashir, B.; Al-Asheh, S.; Hayajneh, O. Adsorption of phenol by bentonite. *Environ. Pollut.* **2000**, *107*, 391−398.