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The effect of ionic environment on the TG response of phenol loaded PET-based porous carbons

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Abstract The effect of the ionic environment on the adsorption of phenol from aqueous solutions was investigated in a microporous carbon and in an oxidized carbon. It was found that not only the pH of the solution but also the method of its setting affects the adsorption capacity. Thermal desorption of phenol exhibits an even stronger dependence on the method of pH setting than adsorption. The TG response, the position and the corresponding TG steps are also influenced by the surface chemistry. Thermogravimetry is found to be outstandingly useful and informative technique for the studying sorption interactions.

Keywords Activated carbon · Adsorption/desorption · pH dependence · Thermal analysis · Surface properties

Introduction

A growing awareness of the potential hazard of pollution by veterinary and human pharmaceuticals in aqueous environments has renewed concern about treatment of both wastewater and drinking water. Although biological methods are the most widely employed, they cannot eliminate non-biodegradable organic, mainly aromatic compounds, which even at low concentration may act as inhibitors for biological treatments. For this reason, adsorption by activated carbons (ACs) is still among the most extensively used technologies, owing to its high affinity for a wide variety of chemicals. Their outstanding performance stems from a unique combination of geometrical and chemical properties. The latter mainly depend on heteroatoms and their chemical forms, which are defined by the origin and the prehistory of the carbon. The most frequent heteroatom is oxygen, which forms various functionalities along the edges of the turbostratic layers. These functional groups and the delocalized electrons of the graphitic structure lend acid/base character to the carbon surface [1–9].

Increased consumption of AC raises the problem of regeneration, not only for financial but also for environmental reasons, because the loaded carbon itself has to be treated as hazardous waste. The feasibility of regeneration depends, among other factors, on the strength of the interactions between the phenol and the carbon surface.

The most commonly used regeneration techniques are based on heat treatment. Thermogravimetric analysis (TG), often combined with further analytical methods, is therefore often employed to study the regeneration process [10–12]. Heat treatment of the phenol loaded carbons in nitrogen atmosphere, for instance, mimics the most commonly used thermal route of carbon regeneration. Adsorption of phenol in activated carbon is a complex process where physical and chemical interactions are involved. During the heat treatment, the adsorbed phenol desorbs only partly, resulting in a carbon-rich residue that remains on the surface of the activated carbon [13]. Phenol desorbed at low temperatures (below 300–400 °C) is considered to be physically adsorbed. When phenol loaded oxidized carbon was studied between 400 and 800 °C only

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one peak was found [14]. The mass loss in this region corresponds to chemically adsorbed phenol, which also can polymerize into compounds of higher molecular mass [13, 15–18]. ^{13}C studies have shown that surface carbon atoms do not participate directly, but catalyze the polymerization of phenol [16]. According to TPD studies on commercial carbons, in most carbons physical adsorption is dominant, although in highly microporous carbons thermal desorption of the physisorbed phenol may be controlled by the width of the narrow pores [14]. The presence of surface oxygen groups has been found to modify the desorption behaviour of the aromatic molecules [19, 20].

In spite of extensive thermal studies, the effect of the medium of the phenol loading on the performance of thermal regeneration has not been systematically studied. However, it is well-known that the aqueous environment may exert a strong influence on the adsorption properties of AC bearing various functional groups [21, 22].

To provide a twofold solution for environmental problems, the ACs reported in this article were produced from poly(ethyleneterephthalate) (PET), which is one of the most common polymers in municipal waste. The influence of the carbon surface chemistry and the aqueous environment under loading on the thermal desorption behaviour of phenol from AC as found by TG is reported.

Experimental

Materials

Microporous granular activated carbon (APET) was prepared from PET pellets by a two-step physical activation method [23]. APETOX was obtained from APET by treatment with concentrated nitric acid for 3 h at room temperature. This sample was then washed with distilled water and extracted in a Soxhlet apparatus until neutral pH was attained.

Methods

Nitrogen adsorption

Nitrogen adsorption/desorption isotherms were measured at 77 K, using a Quantachrome Autosorb-1 computer controlled apparatus. Samples were evacuated at 473 K for 24 h, except those loaded with the phenol, which were treated at room temperature. The apparent surface area S_{BET} was obtained from the BET model. The total pore volume V_{tot} was calculated from the amount of nitrogen vapour adsorbed at a relative pressure close to unity, on the assumption that the pores are then filled with liquid nitrogen. An average pore width d_{ave} ($=2V_{tot}/S_{BET}$) was derived from S_{BET} and the total pore volume V_{tot}, assuming slit-shaped geometry, as revealed by the hysteresis loops. The micropore volume W_0 and the characteristic energy E_0 were deduced from the intercept and the slope of the Dubinin–Radushkevich (DR) plot, respectively ($\beta = 0.389$). The pore width, w, of the slit-shaped micropores is taken to be $2kE_0^{-1}$ ($k = 13$ kJ nm mol^{-1}).

Acid/base characterisation

The carbons were characterized by the pH of their aqueous suspension, detected under standardized conditions [24]. The pH of the point of zero charge pH_{PZC} was measured by the so-called drift method [24, 25]. As the only heteroatom in APET and APETOX is oxygen, the distribution of the functional groups in the different pK_a ranges could be determined by Boehm-titration [6].

Sorption from dilute aqueous solutions of phenols

Phenol (Merck, 99.5%) solutions were prepared using bi-distilled water. For the adsorption isotherms ca. 0.05 g of carbon was shaken with 50 ml of non-buffered phenol (1–10 mM) solutions for 24 h in sealed vials at ambient temperature. The contact times to reach equilibrium were deduced from preliminary kinetic measurements.

To study the influence of pH, phenol-loaded samples were prepared using 5 mM phenol solutions. For one set of samples aqueous HCl or NaOH solutions in the pH range 3–11 were used as solvent. For a second set the phenol was dissolved in Britton-Robinson (BR) buffer solutions in the same pH range. The BR buffers are composed of 0.04 M acetic acid ($pK_a = 4.76$, 25 °C), 0.04 M phosphoric acid ($pK_a = 2.12$, 7.21, 12.76, 25 °C), 0.04 M boric acid ($pK_a = 9.14$, 12.74, 13.80, 20 °C) and 0.2 M NaOH [26].

The initial and equilibrium concentrations c_0 and c_e, respectively, were determined by UV absorption ($\lambda = 265$ nm).The calibration diagrams for UV absorption measurements were determined at each pH for both pH settings.

The linearized Langmuir and Freundlich models were used for data analysis. Although the heterogeneity of the surface sites is in contradiction with the boundary conditions of the Langmuir model, because its parameters have a physical meaning, they are retained for further consideration.

Thermal analysis

Thermal analysis was carried out in nitrogen atmosphere (10 L/min), using a simultaneous DTA-TGA TA Instruments STD 2960 unit. The heating rate was 10 °C/min. Unless otherwise mentioned, the differential thermogravimetric (DTG) curves were used for the analysis.

Table 1 Data from low temperature nitrogen adsorption isotherms

Carbon sample	S_{BET} [m^2/g]	V_{tot} [cm^3/g]	d_{ave} [nm]	w [nm]	E [kJ/mol]	W_0 [cm^3/g]	W_0/V_{tot}
APET	2025	1.02	2.01	1.84	14.1	0.78	0.76
APETOX	2067	1.09	2.12	1.79	14.5	0.80	0.73

Results and discussion

Characterisation of the carbon samples

Low temperature nitrogen adsorption/desorption isotherms were measured to characterize the morphology of the carbons in the nanometre scale region relevant to adsorption interactions. The samples discussed in this paper exhibit Type I isotherms according to the IUPAC classification, showing that both these carbons are mainly microporous. The characteristic parameters of the initial carbons calculated from the isotherms are listed in Table 1.

This set of data indicates that the nitric acid treatment causes no significant change in the surface morphology: APET and APETOX exhibit very similar adsorption properties in dry conditions.

According to the nature of the application, the acid/base properties of the carbons were characterized under wet conditions. The pH_{PZC} and pH (Table 2) indicate that the nitric acid treatment essentially modifies the concentration and the distribution of the surface functionalities (Table 3). The specific amount of oxygen-containing functional groups increases and this results in a significant shift in both the pH and pH_{PZC} values. The concentration of the acidic groups of the APETOX is six times higher than in case of APET, while that of basic groups is halved. While APET contains almost exclusively phenolic acidic groups, the carbonyl, lactone and phenol functionalities are more or less equally abundant in APETOX carbon.

Table 2 pH and pH_{PZC} of the carbon samples

	pH, 25 °C	pH_{PZC}
APET	7.9	9.8
APETOX	3.6	4.2

Influence of carbon surface chemistry and loading in unbuffered systems

The phenol uptake from unbuffered aqueous solutions was measured at room temperature in the equilibrium concentration range 0–8 mmol/L (Fig. 1). The isotherms are of L-type according to Giles's classification. In unbuffered solution both APET and phenol ($pK_a^{20°C} = 9.89$) are more or less in protonated form, as the pH is very close to pH_{PZC}. Below pH_{PZC} the surface is protonated, while at higher pH values it is negatively charged, due to deprotonation. The oxidized carbon surface creates an acidic medium, where the phenol is still protonated, but part of the carbon is deprotonated. The surface functionalization reduces the phenol adsorption capacity by almost 30% because the charged functional groups prevent the π–π interaction between the AC surface and the phenol [21, 27]. The values of the adsorption capacities n_m and the equilibrium constants K from the fit to the Langmuir, and n and K_F from the fit to the Freundlich equations are listed in Table 4.

Although both models gave good fits, n_m from the Langmuir fit was used for further calculations, as it allows an estimation of the surface area occupied by the phenol molecules (assuming that the cross sectional area of phenol is 0.42 nm^2/molecule [28]). Comparison of the surface areas covered by phenol and nitrogen shows that only 44% and 32% are occupied by phenol in APET and APETOX, respectively (Table 4). The surface of both carbon samples is thus only partially covered by the aromatic compound. The reduced access of phenol to the surface sites could be caused by the adsorbed species blocking the pore necks and/or competitive adsorption of the solvent [21, 29, 30].

Loaded carbon samples were air dried prior to the thermal analysis. Air dried APET and APETOX, extracted with water, were used for comparison. As expected, the TG curves of the two pristine carbons have different shapes. The mass loss of APET itself can be neglected in the whole

Table 3 Distribution of surface functional groups

Carbon sample	Acidic groups					Basic groups (μequiv/g)	Total (μequiv/g)
	Carboxyl (μequiv/g)	Lactone (μequiv/g)	Phenol (μequiv/g)	Total acidicity (μequiv/g)	% of the acidic groups		
APET	Below detection limit	5.6	82.6	88.2	27	328.2	416.4
APETOX	197.4	193.8	228.1	619.3	81	148.4	767.7

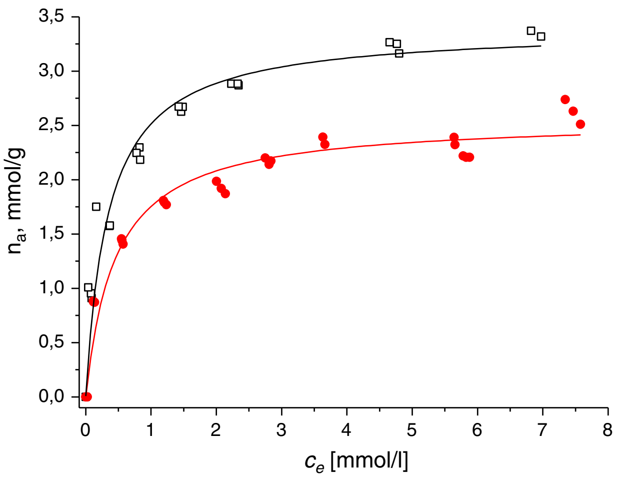

Fig. 1 Adsorption isotherms of phenol from unbuffered solution. (Square) APET, (filled circle) APETOX are the experimental points, lines were fitted to the Langmuir equation

temperature range studied, but APETOX itself exhibits several mass loss steps due to thermal decomposition of the oxygen-containing functional groups (Fig. 2b). Typically, carbonyl groups decompose around 300 °C, lactones around 400 °C, phenol, anhydride, ether, carbonyl and quinone groups between 600 and 900 °C [31]. APETOX exhibited the corresponding peaks at ~296, ~395 and ~690 °C.

As shown in Fig. 2, the shape of the TG responses depends on the carbon adsorbent and the loading concentration. Above 100 °C three different peak regions can be distinguished in the loaded APET carbons, which imply three different types of interaction. Following reference [17], Peak 1 around 210 °C, which is the largest, was attributed to the desorption of physisorbed phenol. The peaks above 300 °C belong to chemisorbed species. Peak 2 appears between 430 and 450 °C, and Peak 3 around 570 °C. Above 350 °C phenol desorbs in various forms:

Table 4 Parameters obtained from the aqueous phenol isotherms

	Langmuir				Freundlich		
	n_m (mmol/g)	K (L/mmol)	R^2	Surface area covered by phenol (m^2/g)	n	K_F	R^2
APET	3.52	2.31	0.998	890	0.32	0.043	0.947
APETOX	2.62	1.92	0.984	663	1.59	3.98	0.957

n_m Adsorption capacity, K equilibrium constant from Langmuir model, n and K_F Freundlich parameters, R regression factor of the linear fits

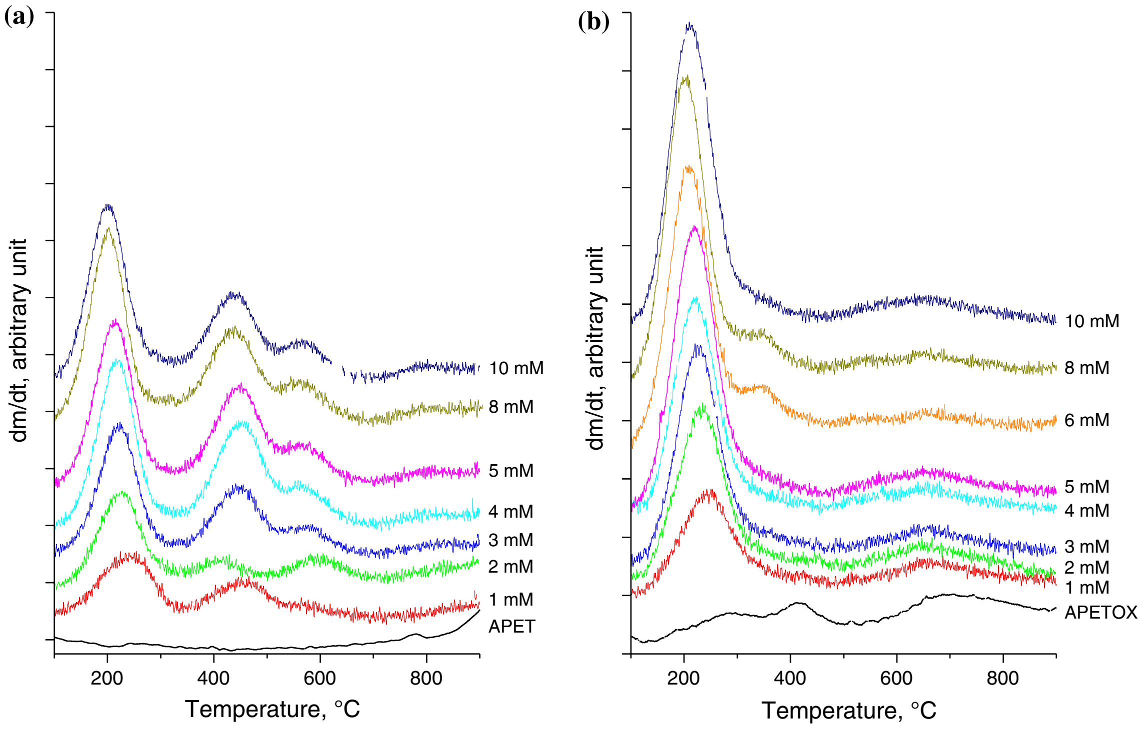

Fig. 2 DTG curves of **a** APET and **b** APETOX loaded from the corresponding phenol solution with the given initial concentrations

phenol, benzyl, furans, fragments and dimers were detected by GC-MS [32].

The loaded APETOX samples gave two peaks (~210 and 650–670 °C). A third peak (~780 °C) was distinguishable only at 6 and 8 mmol/L initial concentrations. Since the size of the peaks at higher temperatures is comparable to the decomposition peaks of pristine APETOX, only the physisorbed peak appearing around 210 °C was further analysed. The intensity of this peak shows that the phenol is mainly physisorbed.

In case of APETOX samples Peak 1 is significantly higher than in the APET samples. In both cases the peak temperatures shifts to lower values as the initial concentration and thus the phenol uptake increases.

The mass loss detected in the different temperature ranges for the two carbons are compared in Figs. 3 and 4. Figure 3 shows that the shape of the "desorption" curves in any of the categories is very similar to the concentration dependence of the phenol uptake. The mass loss attributed to physi- and chemisorbed species is very similar in APET. Altogether, phenol can be removed only partially from the surface, as illustrated by the comparison of the upper two curves in Fig. 3. Depending on the loading concentration, a residue equivalent to 23–35 m/m% of the adsorbed phenol remains deposited on the surface. When the APET is treated with 5 mmol/L phenol, e.g., this deposit reduces the surface area from 2,025 to 1,632 m^2/g.

The first points in Fig. 4 belong to the pristine APETOX carbon losing more than 13% of its mass during the thermogravimetric analysis. The shape similarity was also observed on this sample. The fraction of the physisorbed species is greater in this case. The total mass loss, however, exceeds the amount adsorbed. Functional groups rich in oxygen and/or their decomposition products interact with the phenol and modify the chemical reactions occurring within the pores. The reactions with and CO, CO_2 and further oxygen-containing fragments result in more volatile products and reduce the probability of chemical vapour deposition, i.e., the surface oxygen groups may be considered as self-activators. The regenerated APETOX surface after treatment with 5 mmol/L phenol decreases only to 1,886 m^2/g, because deposition is less favoured.

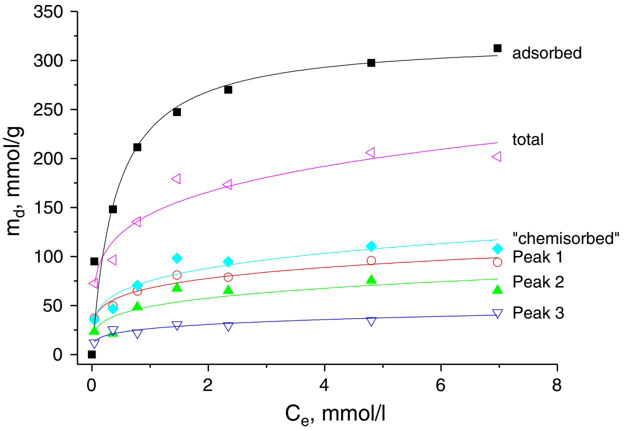

Fig. 3 Phenol uptake and mass loss function of equilibrium concentrations (APET) (Filled square) adsorbed phenol; (circle) Peak 1, (filled triangle) Peak 2, (inverted triangle) Peak 3, (filled diamond) "chemisorbed" (Peak 2 + 3), (arrow head) total mass loss, from measured data, continuous lines are guides for the eye

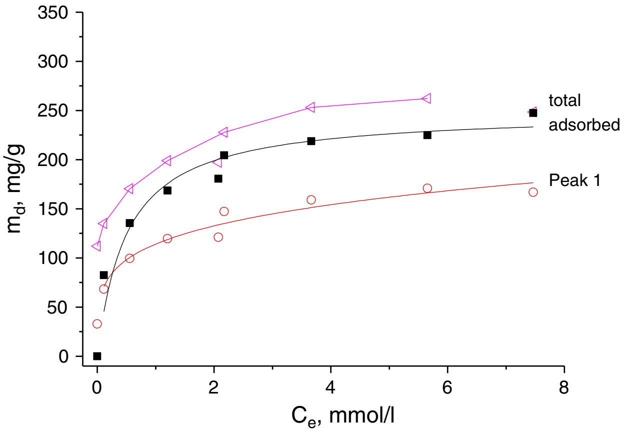

Fig. 4 Phenol uptake and mass loss function of equilibrium concentrations (APETOX) (filled square) adsorbed phenol; (circle) Peak 1, (arrow head) total mass loss measured data, continuous lines are guides for the eye

It can be concluded that the surface chemistry of the carbon controls the adsorption mechanism of phenol. Surface oxidation reduces the adsorption capacity and favours physisorption. The high concentration of surface acidic groups facilitates the thermal regeneration as the oxygen fosters the formation of volatile species at higher temperatures, thus hindering pore blocking through carbon deposition.

Influence of the aqueous medium

The samples for this study were loaded with 5 mmol/L phenol from either HCl/NaOH or BR buffer solutions. The adsorption capacities obtained with the two sets of solutions are listed in Table 5 relative to the uptake measured in the non-buffered (NB) medium**.** For APET the phenol uptake is higher when the pH is set with HCl/NaOH. No systematic pH-dependence was observed and only ~92 ± 5% of the non-buffered capacity was achieved. With the BR buffer a well-defined maximum in the adsorption capacity was detected at pH = 8 and the minimum amount adsorbed was detected at pH = 3. The results in APETOX reveal that the method of pH setting is important only at pH = 3 and above pH = 7, otherwise the uptakes practically equal. APETOX shows higher relative adsorption capacities in BR buffer, which in some cases

Table 5 Equilibrium phenol uptake from 5 mM phenol solutions

	pH	Relative phenol uptake[a], %		Covered by phenol, m^2/g	
		HCl/NaOH	BR	HCl/NaOH	BR
APET	3	93.7	77.5	680	583
	4	93.4	90.1	678	678
	5	86.1	84.9	625	639
	6	93.7	91.1	680	685
	7	94.1	91.1	683	685
	8	99.3	93.8	721	705
	9	92.0	88.7	668	668
	10	85.4	86.6	620	651
	11	92.0	87.8	668	661
	UB[a]	100	100	731	731
APETOX	3	91.9	98.4	513	549
	4	93.1	92.9	520	519
	5	88.2	85.8	492	479
	6	99.9	96.8	557	540
	7	89.8	105.8	501	590
	8	90.9	99.7	507	556
	9	95.4	91.0	532	508
	10	86.1	92.3	480	515
	11	81.1	112.3	452	627
	UB[a]	100	100	567	567

[a] Compared to the adsorption capacity in unbuffered medium

achieves or even exceeds the unbuffered value. From the fact that the acid, base and salt components present in the aqueous phase influence the phenol uptake on APET and APETOX, we can conclude that the salts dissolved in wastewaters may significantly modify the efficiency of the carbon adsorbents used for purification.

The last two columns in Table 5 show that, except in one case, adjusting the pH of the medium, further reduces the surface fraction covered by phenol molecules. Besides the phenol and water, the different ions introduced to set the pH compete for the surface sites. At low pH the surface is protonated, which promotes the interaction with negatively charged dissolved species, while at high pH, when the surface is negatively charged, species with positive charge are preferred. These ions not only occupy surface sites but also may block the pore entrance even for adsorptives that could otherwise have access to the internal surface of the pores.

The result of the analysis of TG curves obtained on APET and APETOX from the two sets of phenol solutions are summarized in Table 6. The mass loss in various temperature ranges were related to the amount of phenol adsorbed from 5 mmol/L solution of the same medium.

The total mass loss was calculated from the value of the 100–900 °C TG curves relative to the adsorbed phenol. "Chemisorbed" was calculated as the difference of this total and the relative mass loss of the phenol desorbed in the 100–300 °C range. As mentioned earlier, loss in the 100–300 °C region is considered as physisorbed phenol, while that in the higher temperature range is derived from chemisorbed species.

In APET samples when the pH is set with acid/base a non-monotonic mass loss was observed. When the pH is set by BR buffer, samples display a systematic change as the pH increases, i.e., the buffer stabilizes the chemistry of the surface processes. The physisorbed step gives a greater mass loss, which decreases monotonically with increasing pH. The relatively sudden drop above the pH_{PZC} may stem from reduced physisorption due to electrostatic repulsion. The physisorbed and the "chemisorbed" amounts are practically equal at $pH = 11$. A carbon rich residue equivalent to 10–35% of the adsorbed phenol remains on the surface.

In case of APETOX samples with HCl/NaOH pH setting, the loss is almost constant (first peak: $\sim$70%, total $\sim$110%), although it has a minimum at $pH = 6$. The TG curves of the BR buffered samples display again a systematic change with increasing pH. That is, similarly to APET, the buffer stabilizes the chemistry of the surface processes. From APETOX the total mass loss exceeds the adsorbed amount, due to the increased reactivity of the functional groups, as mentioned already in case of the unbuffered samples. As a general trend, it can be concluded that the mass loss related to chemisorbed species increases with the pH.

The surface area values of the carbons loaded at $pH = 3$ and 11 (Table 7) show that the morphology changes both in the adsorption and the thermal treatment step. The adsorbed phenol and other species—as was expected—reduce the surface area by filling the pores, although the extent of the surface loss depends on the aqueous environment. The only exception is APET loaded at pH 11 from NaOH solution. NaOH is a well-known chemical activating agent, which in the dry state may react with the non-oxidized carbon surface and modify the porosity [33]. This oxidative effect is suppressed when the surface is already oxidized.

Heat-treatment removes part of the adsorbed phenol, but the oxygen introduced by the phenol may play the role of an activating agent and the deposition of carbon-rich residue leads to the development of new pores. Both processes result in an increase in the surface area. In the APETOX samples the surface oxygen groups play a similar activating role, which in this case may help remove the adsorbed phenol in a more volatile form. This results in a limited change in the surface area. The activating ability of NaOH is also shown in both heat-treated carbons after loading from NaOH at pH 11. Otherwise, the slight surface

Table 6 Relative mass loss respect to the adsorbed phenol, %

	pH	APET			APETOX		
		First peak 100–300 °C	Total 100–900 °C	Chemisorbed[a] 300–900 °C	First peak 100–300 °C	Total 100–900 °C	Chemisorbed[a] 300–900 °C
HCl/NaOH	3	60.0	80.7	20.7	75.2	109.5	34.3
	4	32.3	72.1	39.8	71.8	111.6	39.8
	5	45.1	72.9	27.8	68.4	107.0	38.6
	6	50.8	84.5	33.7	62.9	100.7	37.8
	7	42.5	75.7	33.1	66.0	104.7	38.7
	8	24.2	62.7	38.5	69.5	109.5	40.0
	9	25.6	65.1	39.4	67.2	108.5	41.3
	10	29.2	74.6	45.4	68.3	110.8	42.5
	11	43.4	75.6	32.2	71.2	116.0	44.8
BR	3	84.5	89.7	5.2	74.4	120.5	46.1
	4	74.9	80.7	5.9	70.2	119.6	49.4
	5	73.5	81.0	7.5	71.0	124.9	53.9
	6	65.3	79.2	13.9	61.8	108.1	46.3
	7	60.8	78.2	17.4	55.1	103.2	48.1
	8	54.8	75.4	20.6	59.9	110.7	50.8
	9	43.7	68.6	24.9	45.7	104.3	58.6
	10	36.6	64.1	27.5	35.1	95.9	60.8
	11	31.2	59.9	28.8	21.6	78.7	57.1
UB[b]		34.0	64.7	30.6	77.3	111.4	34.1
Carbon[c]		–	100	–	15.0	100.0	85.0

$\frac{\text{Mass loss in the given temperature interval}}{\text{Total adsorbed phenol}} \times 100, \%$

[a] Chemisorbed = Total − Physisorbed

[b] Unbuffered samples

[c] Air dried carbons, washed with bidistilled water

Table 7 Surface area of the loaded and regenerated samples

	pH	APET		APETOX	
		Phenol loaded	After heat treatment	Phenol loaded	After heat treatment
HCl/NaOH	3	1,352	2,306	890	1,897
	11	2,136	3,648	1,222	2,407
BR	3	1,272	2,764	1,087	2,141
	11	1,716	2,706	1,145	1,948
UB[a]		1,541	1,632	792	1,886
Initial		2,025		2,067	

[a] Unbuffered sample

reduction in the APETOX carbon is apparently independent of the previous aqueous history of the sample.

Conclusions

In this paper factors influencing the thermal regeneration of carbon adsorbents were studied, namely (i) the surface chemistry of the carbon adsorbent, (ii) the phenol concentration of the loading solution, (iii) the pH of the solution, (iv) the method of pH setting. All these factors were found to influence the surface area of the carbons recovered after the thermal treatment.

- The surface chemistry of the carbon controls the adsorption mechanism of phenol. Surface oxidation reduces the adsorption capacity and favours physisorption. The high concentration of surface acidic groups facilitates the thermal regeneration as the oxygen fosters the formation of volatile species at higher temperatures, thus hindering pore blocking through carbon deposition.

- From the finding that the acid, base and salt components present in the aqueous phase influence the phenol uptake on APET and APETOX, we can conclude that the salts dissolved in wastewaters may significantly modify the efficiency of the carbon adsorbent used for purification.
- The surface area of the thermally regenerated samples depends strongly on the previous aqueous history of loading. With unbuffered solutions only part of the surface area can be regained. When physisorption is dominant no significant change in the surface area was observed. NaOH alone, through the chemical activation, results in a significant increase in the surface area of the regenerated carbon.

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