

REMOVAL OF A DIOXIN MODEL COMPOUND IN AQUEOUS SOLUTION BY ADSORPTION ON ACTIVATED CARBON

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Introduction

Dioxins are highly toxic persistent organic pollutants, produced by many industrial processes and by some natural processes (such as forest fires). These compounds tend to accumulate in the environment, being necessary to control their emission.

The aim of this work was to study the adsorption of dioxins on activated carbons, using a model compound. The chosen model compound was 2',7'-dichlorofluorescein due to its structural similarity to dioxins.

Experimental

A commercially activated carbon supplied by Norit (Norit Gac 1240 Plus) was used as the starting adsorbent material. The parent sample was treated in order to modify the surface chemistry (Table 1).

Oxidation was performed by contacting HNO₃ (6M) at room temperature during 24h.

Nitriding was carried out at 523K (2,5hr) flushing gaseous ammonia (F=2,5cm³/s) which was obtained by evaporation of liquid ammonia at ambient conditions.

Prior to use, the oxidized and nitrided samples (C1 and C3, respectively) were washed until neutral pH and dried at 363 K.

Devolatilization of the carbon was achieved by heat treatment in nitrogen at 1073 K during 2h.

Table 1. Surface modifications applied to the starting material.

Sample	Starting Material	Conditions
C0	—	Norit Gac 1240 Plus
C1	C0	HNO ₃ 6 M, room temperature, 24 h
C2	C0	N ₂ , 1073K, 2 h
C3	C0	NH ₃ , 523K, 2,5 h

These materials were characterized by nitrogen adsorption at 77 K (Micromeritics ASAP 2010), temperature-programmed desorption (TPD, Micromeritics TPD/TPR 2900), elemental analysis (Thermo Finnigan – CE Instruments Elemental Analyser 1112 series) and X-ray photoelectron spectroscopy (XPS, XSAM800).

The pH_{PZC} of all the samples was measured by mass titration.

The pK_a values of the model compound were determined recording absorption spectra on a Shimadzu UV-2510 PC, UV-vis spectrophotometer, and recording fluorescence emission on a SPEX F111 Fluorolog spectrofluorimeter. HCl and NaOH were used to adjust the pH values that were measured on a Metrohm 713 pH meter.

Batch adsorption isotherms of 2',7'-dichlorofluorescein were obtained by adding 200ml of an aqueous solution using different known concentrations (0,5 – 5 ppm) to 0,02 g of carbon. The pH of the solutions was not adjusted ($\text{pH}_{\text{initial}}=5,7$). These suspensions were shaken for 22 days in an ellipsoidal shaker at a stirring rate of 170 r.p.m. The equilibrium concentrations were measured by UV Spectroscopy (GBC UV/VIS 916) at 502 nm, adjusting pH values to 12 with NaOH.

Results and Discussion

Table 2 and 3 summarize some of the physical and chemical characteristics of the samples used.

Table 2. Textural characteristics of the studied activated carbons.

Sample	$S_{\text{N}_2}^{\text{a}}$ (m^2/g)	$V_{\text{micro}}^{\text{b}}$ (cm^3/g)	$S_{\text{ext}}^{\text{b}}$ (m^2/g)	pH_{PZC}
C0	1199	0.39	94	8.8
C1	1212	0.40	96	3.1
C2	1206	0.40	94	9.8
C3	1151	0.38	90	9.5

^a Apparent specific area.

^b Micropore volume and external surface area obtained by application of the t-method to the N_2 adsorption isotherm, considering the standard adsorption isotherm proposed by Rodriguez-Reinoso *et al* [1].

Table 3. Elemental Analysis and XPS of the studied activated carbons.

Sample	Elemental Analysis (wt%)					XPS (wt%)				XPS/EA ^a	
	C	N	H	S	O	C	N	S	O	N	O
C0	84.83	0.93	0.52	0.53	13.19	77.08	1.70	0.57	20.65	1.83	1.57
C1	78.67	0.63	0.53	0.44	19.73	63.37	4.25	0.35	32.08	6.74	1.63
C2	86.65	0.44	0.36	0.55	12.00	77.35	1.78	0.76	20.11	4.05	1.68
C3	85.39	0.59	0.38	0.56	13.08	72.99	1.76	0.50	24.75	2.98	1.89

^a XPS/EA calculated by the ratio between XPS and Elemental Analysis values for nitrogen and oxygen, respectively.

No drastic changes in surface area and micropore volume were observed, in agreement with previous studies [2,3].

The values obtained for pH_{PZC} show that oxidation increases surface acidity, while heat treatment and ammonia treatment increase slightly surface basicity.

Table 3 shows that oxidation with HNO_3 slightly increases the oxygen content. The higher content observed for nitrogen, may be due to the presence of nitric acid inside the pores that was not totally removed during washing.

The oxygen content of the devolatilized sample (C2) probably reflects reoxidation of the surface by exposure to atmosphere during sample handling.

The nitrated sample does not exhibit a higher amount of N incorporated as we were expecting, but the results obtained by XPS suggest that the treatment introduce amine or amide groups (~ 399.5 eV).

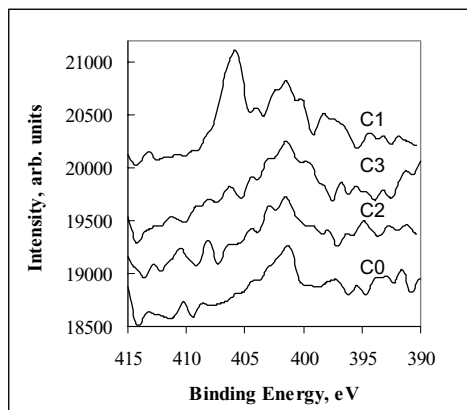


Figure 1. The N1s signals of the samples C0, C1, C2 and C3.

TPD results indicated that oxidation with HNO_3 , increases the amount of oxygen surface groups. It was observed an increase of CO_2 evolution attributed to the presence of carboxylic groups, carboxylic anhydrides and lactones. The CO evolution showed an increase on phenols and quinones as well as in anhydrides.

The CO_2 evolution of the heat treated sample showed a decrease in carboxylic and lactone groups when compared to the parent sample, although it was observed a slight increase for phenols.

As explained elsewhere [2,4], the adsorption of aromatic compounds is determined by electrostatic and dispersive interactions. Thus, the adsorption of 2',7'-dichlorofluorescein on activated carbon is strongly influenced by its pK_a , pH of the solution and carbon pH_{PZC} , among other factors.

The obtained pK_a values for 2',7'-dichlorofluorescein were 4,4 and 8,5, indicating that the model compound will be deprotonated in solution, since the initial pH of the solution was 5,7. After reaching the pseudo-equilibrium the pH of the solution was 7,2.

Figure 2 presents the pseudo-equilibrium adsorption isotherms for 2',7'-dichlorofluorescein. It was observed some data dispersion, which suggests the existence of mass transfer limitations. In order to describe the adsorption data, Langmuir and Freundlich models were used.

The devolatilized and nitrated carbons exhibited the highest uptakes. In contrast, carbon oxidation decreases 2',7'-dichlorofluorescein adsorption capacity.

For the oxidized sample the pH of the solution is higher than the pH_{PZC} , indicating that carbon surface is charged negatively. As the adsorbate is dissociated, there are electrostatic repulsions that unfavour adsorption. Furthermore, surface oxygen complexes also affect the electronic density of the graphene layers, which decrease dispersive interactions.

In the case of samples C0, C2 and C3 the pH of the solution is lower than pH_{PZC} and the surface charge is predominantly positive. Due to the negative charge of the adsorbate there are adsorbate/adsorbent electrostatic attractions.

Comparing samples C0, C2 and C3 we observe that sample C2 contains less oxygen- and nitrogen functional groups, which increases π electron density in the graphene layers, favouring $\pi-\pi$ interactions.

Apart from these two adsorption mechanisms, it is also important to consider the existence of hydrogen bonds between the model compound and adsorbent surface groups.

Dioxins do not have deprotonable groups in its chemical structure, having low solubility, which determines hydrophobic interactions.

Further studies will be carried out using solutions with adjusted pH, lower than $pK_{a1}=4,4$, in order to simulate dioxins behaviour.

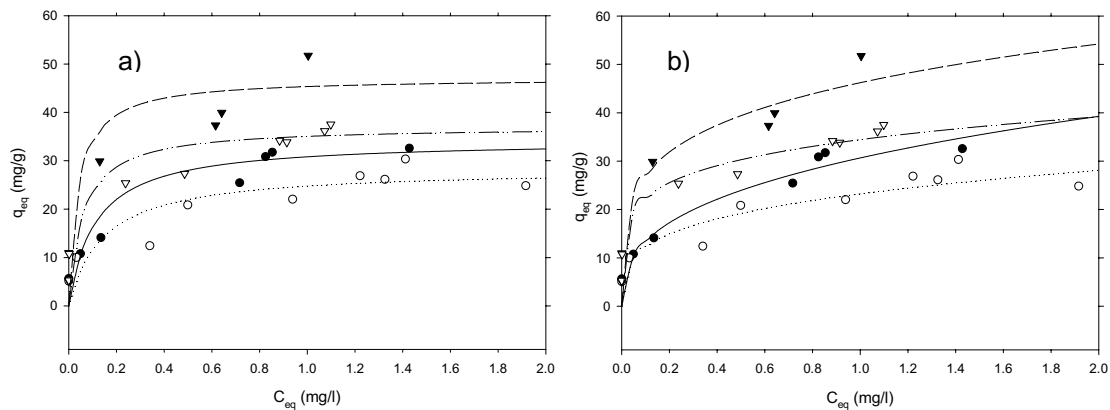


Figure 2 - Pseudo-equilibrium adsorption isotherms for 2',7'-dichlorofluorescein: a) experimental data and Langmuir model fitting; b) experimental data and Freundlich model fitting. ● C0; ○ C1; ▼ C2; ▽ C3.

Conclusions

The adsorption of 2',7'-dichlorofluorescein seems to be affected by the surface and solution chemistry. The results suggest that the adsorption of dioxins should be enhanced using hydrophobic adsorbents.

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