Comparative adsorption of levodopa from aqueous solution on different granular activated carbons

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Introduction

❖The occurrence of pharmaceuticals in the aquatic environment is a rising problem

❖The threefold increase in drug consumption in the next 22 years will make it even more critical

❖Considering the potential impacts of pharmaceutical products, it is highly important to remove them from wastewater before discharge.

❖Levodopa: One of the several drugs used to control symptoms of Parkinson's disease

❖Great influence of chemical surface composition on adsorption mechanism.

Goals: * Determination of adsorption isotherms of levodopa from aqueous solution onto three activated carbons.

*** Evaluation of five models to fit the experimental data.**

*** Relationships between chemical composition of carbon's surface and adsorption**

Experimental

Adsorption conditions: Temperature: 25°C (thermostated bath). Time: 18 h.
100 mL of solution (initial concentration between 0.031g/L and 1.281 g/L)
Three activated carbons (ACs) from different source materials:

- Coconut shell carbon: S23 (0.05 g)
- Wood carbon: L27 (0.1 g) :
- Casuarina carbon: C1 (0.05 g)

Analysis: HPLC-UV (wavelength 278 nm), C18 reverse phase column (ProtonSIL C18 AQ), eluent: water-acetonitrile (90:10), 0.25 mL/min

Activated Carbons characterization: Nitrogen sorptometry (ASAP 2010 analyzer).
Thermogravimetric analysis (TGA): N_2, T: 20-700°C (10°C/min)
Surface groups determination by Boehm method
Point of cero charge (pH pzc)

Properties	Specific surface area $m^2.g^{-1}$	Microporous volume* $cm^3.g^{-1}$	Mesoporous volume** $cm^3.g^{-1}$	C_a mmol. g^{-1}	C_b mmol. g^{-1}	Total surface groups (C_a + C_b) mmol. g^{-1}	pH_{PZC}
L27	1860	0.77	0.48	2.108	0.798	2.906	6-6.2
S23	1175	0.47	0.05	0.397	0.958	1.355	9-9.1
C1	1230	0.53	0.26	0.125	2.125	2.25	11

* calculated from Horvath-Kawazoe model
** calculated from Barret-Joyner-Halenda method

Results and Discussion

Adsorption isotherm models

Model	Equation
Langmuir	$q = (q_{max}\ KC\ )/(1 + KC\ )$
Jovanovic	$q = q_{max}\ (1 - e^{-(KC\ )})$
Freundlich	$q = K\ (C\ )^{\gamma}$
Redlich-Peterson	$q = (aKC\ )/(1 + K\ (C\ )^{\gamma})$
Khan	$q = (aKC\ )/(1 + KC\ )^{\gamma}$

q: weight of adsorbed compound at equilibrium per unit weight of AC; qmax: monolayer capacity; C: concentration of adsorbate in aqueous phase at equilibrium; γ, K, and a are model parameters.

Optimization: non linear regression (method of least squares).

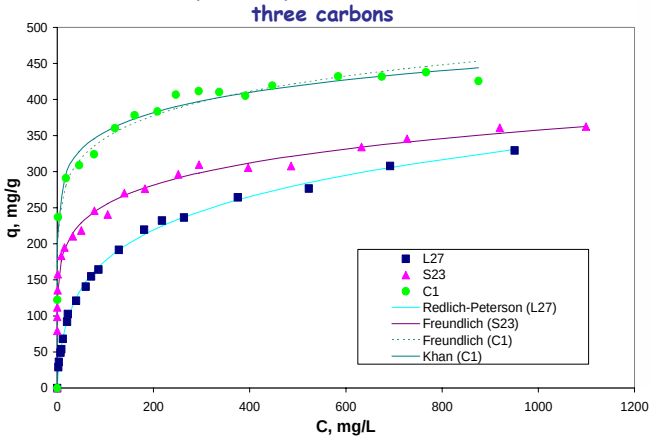
Parameters	L27 Carbon	S23 Carbon	C1 Carbon
1- Langmuir			
q_{max} (mg/g_{AC})	317.9 ± 24.6	285.3 ± 26.4	393.3 ± 23.8
K (L/mg)	0.015 ± 0.004	1.12 ± 0.84	0.88 ± 0.69
RSS	5352	44384	26380
AIC_c	116.5	172.0	136.0
AARE	17.6	16.5	10.3
2- Freundlich			
K ($mg^{1-\gamma}.L^{\gamma}.g_{AC}^{-1}$)	35.1 ± 6.1	128.0 ± 8.6	196.1 ± 20.7
γ (-)	0.34 ± 0.03	0.15 ± 0.01	0.12 ± 0.02
RSS	3190	2759	5086
AIC_c	106.1	110.9	106.4
AARE	13.7	5.4	5.1
3- Jovanovic			
q_{max} (mg/g_{AC})	278.5 ± 26.6	278.4 ± 27.8	388.1 ± 26.2
K (L/mg)	0.012 ± 0.004	0.99 ± 0.63	0.67 ± 0.44
RSS	12969	53866	33966
AIC_c	134.2	176.3	140.6
AARE	24.8	18.6	12.2

Parameters	L27 Carbon	S23 Carbon	C1 Carbon
4-Redlich-Peterson			
a ($mg^{\gamma}.L^{1-\gamma}.g_{AC}^{-1}$)	72.3 ± 12.3	132.9 ± 14.0	224.3 ± 24.8
K ($L^{\gamma}.mg^{-\gamma}$)	0.18 ± 0.07	28.5 ± 66.3	5.6 ± 4.4
γ (-)	0.77 ± 0.03	0.86 ± 0.02	0.90 ± 0.02
RSS	383	2616	2566
AIC_c	66.6	112.5	97.0
AARE	4.1	5.1	3.1
5-Khan			
a (mg/g_{AC})	108.1 ± 20.7	84.1 ± 35.1	187.3 ± 37.1
K (L/mg)	0.10 ± 0.04	25.4 ± 52.1	5.5 ± 4.3
γ (-)	0.75 ± 0.03	0.86 ± 0.02	0.90 ± 0.02
RSS	478	2569	2465
AIC_c	71.0	112.1	96.3
AARE	4.7	5.0	3.0

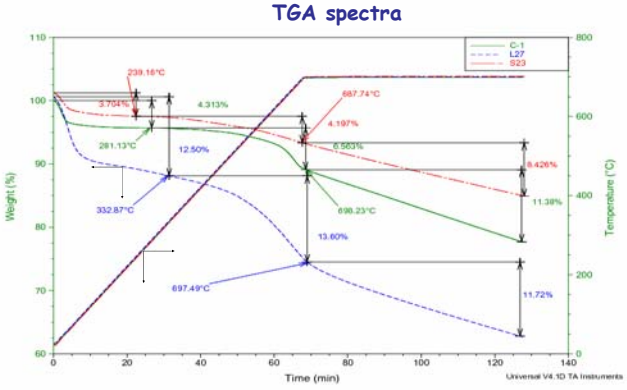
AICc: the corrected Akaike information criterion

AARE: average of absolute relative errors

Levodopa adsorption isotherms for the three carbons



TGA spectra



They reveal a distinct behaviour of L27 carbon and confirm the results of Boehm titration with an increasing weight loss from S23, C1 to L27 AC. .

Conclusions

The adsorption of levodopa is clearly disfavored by the presence of acidic groups as lower levodopa uptake is found with L27 AC despite a higher surface area. Comparing C1 and S23 ACs which have similar specific surface area (and low amounts of acidic surface groups), it is observed that the adsorption capacity is positively influenced by the presence of basic surface groups. While the surface of L27 may be essentially in the neutral form (pH ≈ pH_{PZC}), the surface of S23 and C1 carbons is positively charged (pH < pH_{PZC}), which contributes to enhance adsorption of levodopa which has a 1st pK_a value equal to 2.3 (corresponding to COOH function) and is partially dissociated in the solution (pH > pK_{a1})

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