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Comparative adsorption of levodopa from aqueous solution on different activated carbons

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ABSTRACT

Adsorption on activated carbon has been successfully used in wastewater and drinking water treatment plants for the removal of various pollutants. Among them, pharmaceutical compounds have become a growing issue. The present study has focused on levodopa molecule, which is one of the drugs used to treat symptoms of Parkinson's disease. The adsorption of levodopa onto three activated carbons from different source materials is reported for the first time and analyzed according to both textural and surface chemical properties of the carbons.

The activated carbons are characterized using low temperature nitrogen adsorption, thermogravimetry analysis and Boehm titration. The equilibrium isotherms are measured at 25 °C and five models (Langmuir, Jovanovic, Freundlich, Redlich–Peterson and Khan) are evaluated to fit the experimental data. The characteristic parameters of each isotherm model are optimized and the selection of the most adequate one is performed using statistical regression criteria. For two of the studied carbons the adsorption process can be well described by Freundlich model with an average relative error of 5%, while for the last carbon only three-parameter models gives good fitting.

1. Introduction

Although the presence of drugs in waterways has been established for almost 30 years, there have been only few attempts to evaluate the occurrence, fate and effects of pharmaceutical residues on the environment until fairly lately [1].

In comparison to traditional pollutants, such as PCBs and dioxins, pharmaceutical substances are developed to produce a biological response and are used in high volumes [2]. Most drugs are designed so that they retain their chemical structure long enough to do their therapeutic work and this property, combined with their continuous input, may enable them to remain in the environment for extended periods of time [3]. The possibility for continual but undetectable or unnoticed effects on aquatic organisms is particularly worrisome because effects could accumulate so slowly that major change goes undetected until the cumulative level of these effects finally cascades to irreversible change [4].

Considering the potential impacts of pharmaceutical products on environment and human health, it is highly important to remediate them from wastewater before discharge. Several researches have shown that many pharmaceutical compounds are not completely removed by conventional wastewater treatment (e.g. activated sludge) and, as a result, their occurrence is being reported in sewage plant effluents, rivers, lakes and, more rarely, in groundwater [5,6]. Ninety-five organic wastewater contaminants including pharmaceutical compounds have been recently detected in 139 streams across the USA [7].

Therefore, it is essential to install additional treatment processes. Activated carbon (AC) adsorption has already been successfully used in wastewater and drinking water treatment plants, to remove different pollutants, such as surfactants, pesticides, dyes, and aromatic compounds.

Extensive experimental and modeling studies have been reported on the AC adsorption of a broad spectrum of hazardous compounds from aqueous solution [8,9]. Specifically, the adsorption of different pharmaceuticals has become one of the aims of the researchers in the world. Several common pharmaceutical products like paracetamol [10–12], aspirine [13], theophylline [14], estrone and 17β-estradiol [15,16] have been studied. The authors have investigated the role of different (environmental or adsorbent) parameters on the adsorption of those molecules on activated carbons. Interfering substances found in natural water or sewage treatment plant effluent (like surfactants and humic acids) strongly affect the adsorbability of the drugs, due to solubilization, site

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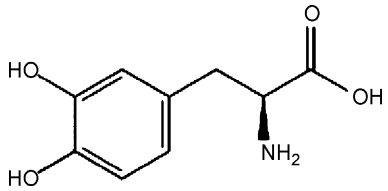

Fig. 1. Molecular structure of levodopa.

competition and/or pore blockage effects [15,16]. Apart from their specific area [16], the chemical surface composition of the activated carbons, i.e. the content of both acidic and basic functional groups, also influence their adsorption capacity for biologically active compounds [10–12].

Adsorption isotherms are normally developed to evaluate the capacity of activated carbons for the adsorption of a particular molecule. They constitute the first experimental information, which is generally used as a tool to discriminate among different ACs and, thereby, to choose the most appropriate one for a particular application [17].

Adsorption mechanisms are so complicated that no simple theory can adequately represent all experimental data. Many expressions have been published to describe the equilibrium relationship between the sorbate and the adsorbent. Langmuir and Freundlich isotherms are the most common ones [18].

Levodopa, a phenolic compound (Fig. 1), is the most frequently prescribed drug for the treatment of Parkinson's disease [19]. Its occurrence in the environment has not yet been reported, but it has been identified in the effluents of a formulation plant in Cuba [20]. The levodopa effect on cell death by oxidative stress and its neurotoxicity for animals have been demonstrated [21]. The goal of this study is to determine the adsorption isotherms of levodopa on three different ACs at 25 °C and to model the corresponding data. A first attempt is made to determine the influence of carbon surface chemistry on levodopa adsorption. Observed trends are also compared to the case of other phenols reported in literature.

2. Experimental

2.1. Materials

Levodopa (>99% purity) has been purchased from Sigma–Aldrich. Levodopa solutions are prepared from a stock solution and deionised water. The other chemicals used for carbon surface group analysis have been purchased from Merck. Activated carbons (ACs) from different source materials are used as adsorbents: L27 from wood (PICA), S23 from coconut shell (PICA) and C1 (CIPIMM) from casuarine. The particle size of ACs is in the range of 0.2–0.4 mm in all cases.

2.2. Physical and chemical properties of carbons

2.2.1. Specific surface area and pore volume

The surface area and pore volume of the carbons are measured from nitrogen adsorption isotherms at 77 K, using an ASAP 2010 analyzer (Micromeritics). Specific surface area is calculated from BET plot for relative pressures between 0.01 and 0.2 [22].

2.2.2. Thermal analysis

Thermogravimetry analysis (TGA) has been performed under nitrogen flow from room temperature to 700 °C with a heating rate of 10 °C/min (Q600 SDT, TA Instrument) in order to compare the amount of functional groups on the three carbons.

Table 1
Adsorption isotherm models: q is the amount of adsorbed compound at equilibrium per unit amount of adsorbent, q_{max} is the monolayer capacity, C is the concentration of adsorbate in aqueous phase at equilibrium, γ, K and a are model parameters.

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	$q = (aKC)/(1 + KC)^{\gamma}$

2.2.3. Surface group determination

The acid/base properties of ACs have been determined using the procedure proposed by Boehm [23]. 70 mL of 0.05N NaOH or 0.05N HCl solutions are added to 1 g of AC in a glass bottle. The bottles are degassed under N_2, sealed and allowed to equilibrate for 3 days in a rotatory shaker. Then, the carbon is separated from the solution and 3 mL of each filtrate are titrated (DL 50, Mettler Toledo) using HCl or NaOH (0.05N), as required. Each experiment is triplicated under identical conditions.

2.3. Point of zero charge (PZC) measurements

To quantify the pH at the point of zero charge (pH_{PZC}), 0.1 g of carbon has been added to 20 mL of 0.1 mol/L NaCl solution, whose initial pH has been adjusted with NaOH or HCl. The containers are flushed with N_2, sealed and placed in a shaker for 24 h, after which the pH is measured. The PZC occurs when there is no change in the pH after contact with the carbon.

2.4. Adsorption isotherm measurements

Equilibrium adsorption experiments have been carried out to evaluate the adsorption capacity of the adsorbents. In a single experiment, 100 mL of a levodopa solution (initial concentration between 0.031 and 1.281 g/L) and a fixed amount of activated carbon (0.1 g for L27 and 0.05 g for S23 and C1) are mixed during 24 h in a thermostated bath at 25 °C. The concentration of levodopa in solution is measured by HPLC using a C_{18} reverse phase column (ProntoSIL C18 AQ) and a Varian ProStar 310 UV/Vis detector (wavelength 278 nm). The equilibrium concentration of levodopa on solid phase is calculated from initial and final concentrations in aqueous solution. Each experiment is repeated threefold under identical conditions.

In this work, the pH of the solutions is left free during adsorption experiments, leading to slightly acidic solution in the pH range 5.5–6.5.

2.5. Adsorption modeling

Five different models are used to fit single-component isotherms (Table 1). Some of those models have been originally proposed for the treatment of gas mixtures; however, their application to liquid mixtures is supported by theoretical and practical reasons [24]. They can be classified into:

- two-parameter isotherm models for homogeneous surfaces without lateral interactions, like Langmuir equation [25] and Jovanovic equation [26];
- two-parameter isotherm models for heterogeneous surfaces without lateral interactions, like Freundlich equation [27];
- other empirical isotherm models for heterogeneous surfaces, like Redlich–Peterson equation [28] and Khan equation [18] (three-parameter models).

Table 2
Physical and surface chemical properties of the activated carbons. C_a and C_b are the total concentrations of acidic and basic groups per gram of activated carbon.

Properties	Specific surface area (m^2/g)	Microporous volume[a] (cm^3/g)	Mesoporous volume[b] (cm^3/g)	C_a (mmol/g)	C_b (mmol/g)	Total surface groups ($C_a + C_b$) (mmol/g)	pH_{PZC}
L27	1860	0.77	0.48	1.85	0.59	2.44	6.2
S23	1175	0.47	0.05	0.30	0.98	1.28	9.7
C1	1230	0.53	0.26	0.125	2.125	2.25	11

[a] Calculated from Horvath–Kawazoe model.
[b] Calculated from Barret–Joyner–Halenda method.

Redlich–Peterson isotherm incorporates the features of both Freundlich and Langmuir isotherms. It is similar to Henry isotherm at low concentrations, and behaves like Freundlich equation for high concentrations.

Khan equation is also a generalized model which can represent both extremes, Langmuir- and Freundlich-type. It was developed for both multi-component and single-component adsorption systems.

Fitting of the adsorption isotherm models to the experimental data is performed using a non-linear regression algorithm (trust region method). The procedure calculates the values of the isotherm parameters which minimize the residual sum of squares (RSS):

$$\mathrm{RSS} = \sum_{i=1}^{n} (q_{\mathrm{exp},i} - q_{t,i})^2 \quad (1)$$

where $q_{\mathrm{exp},i}$ and $q_{t,i}$ are the experimental and calculated values for each data point, respectively.

The best fitting model is chosen according to statistical regression criteria: 95% confidence intervals of parameters, Akaike information criterion (AIC) and average of absolute relative errors (AARE).

The AIC methodology [29] attempts to find the model that best explains the data with a minimum of free parameters. Assuming that model errors are normally and independently distributed, the AIC is defined by the following equation:

$$\mathrm{AIC} = n \cdot \ln\left(\frac{\mathrm{RSS}}{n}\right) + 2k \quad (2)$$

where k is the number of parameters in the model, and n is the number of data points.

The preferred model is the one with the lowest AIC value.

When n is small compared to k, the second-order corrected AIC value ($\mathrm{AIC_c}$) is more accurate:

$$\mathrm{AIC_c} = \mathrm{AIC} + \frac{2k(k+1)}{n-k-1} \quad (3)$$

The average of absolute relative errors is calculated as:

$$\mathrm{AARE} = \frac{100}{n} \cdot \sum_{i=1}^{n} \frac{|q_{\mathrm{exp},i} - q_{t,i}|}{q_{\mathrm{exp},i}} \quad (4)$$

3. Results and discussion

3.1. Textural and surface chemical properties of carbons

Table 2 shows the textural and surface chemical properties of the carbons. Among the investigated ACs, L27 has the highest surface area. S23 and C1 have very similar surface area but S23 is essentially a microporous carbon. The quantification of the carbon surface groups by Boehm titration reveals that L27 has also the greatest content of acidic and total surface groups. On the other hand, C1 has the greatest content of basic groups. TGA spectra (Fig. 2) confirm the results of Boehm titration with an increasing weight loss from S23, C1 to L27 AC.

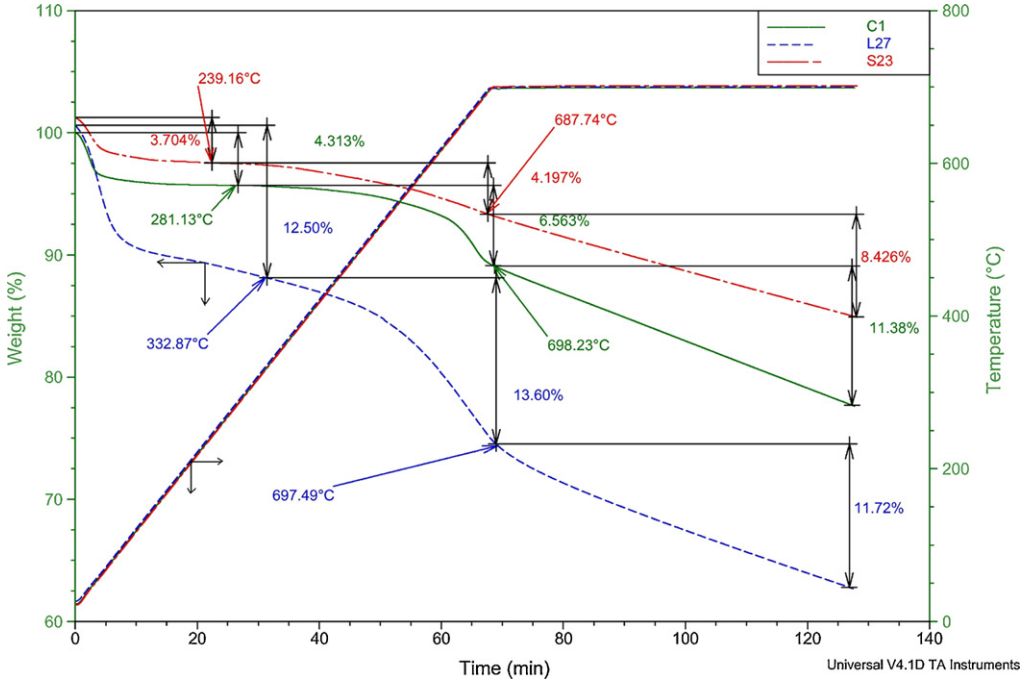

Fig. 2. TGA spectra of L27, S23 and C1 carbons at 25 °C.

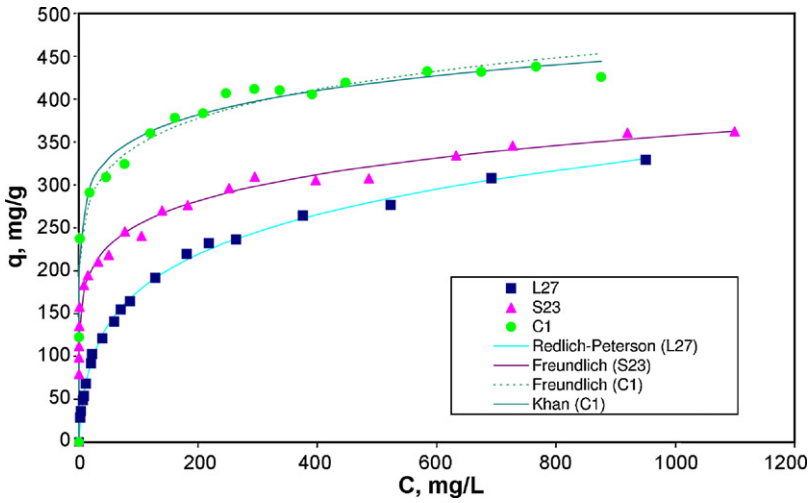

Fig. 3. Adsorption isotherms of levodopa on L27, S23 and C1 carbons at 25 °C. q is the amount of adsorbed compound at equilibrium per unit amount of adsorbent (mg/g_{AC}); C is the concentration of adsorbate in aqueous phase at equilibrium (mg/L).

3.2. Adsorption of levodopa

3.2.1. Role of surface chemistry

The experimental adsorption data of levodopa on L27, S23 and C1 activated carbons at 25 °C are plotted in Fig. 3. The average relative error of the measured concentrations in the liquid phase is 3.4%. The isotherms show that C1 has the greatest adsorption capacity even if it has not the greatest surface area. This result illustrates that no simple relation exists between the adsorption capacity of carbons and their textural properties; this has also been reported by Moreno-Castilla [17], who has shown that the surface chemistry of the carbon has to be considered an important factor in the adsorption mechanism from diluted aqueous solutions.

Several works have been conducted in order to elucidate the mechanism of adsorption of many molecules on different adsorbents. Those publications reveal that adsorption of organic molecules from dilute aqueous solutions on carbon materials is a complex interplay between electrostatic and non-electrostatic interactions and that both interactions depend on the characteristics of the adsorbent and adsorbate, as well as the solution chemical properties [17].

The adsorption of levodopa appears here to be clearly disfavored by the presence of acidic groups as lower levodopa uptake is found with L27 AC despite a higher surface area. This result is in accordance with those obtained for phenol and some aromatic molecules for which a clear decrease in adsorption capacity is found when there are more acidic groups on the carbon surface [30,31]. An accepted mechanism for this phenomenon is the formation of water clusters, particularly with carboxylic groups, through H-bonding which reduces the adsorption capacity [31].

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. The positive effect of basic groups on the carbon surface – via donor–acceptor interactions or chimisorption (oxidative coupling) – is well documented in the case of phenol (the most studied molecule) and some other phenolic compounds [32]. However Terzyk [10] has reported in neutral pH conditions a decrease of paracetamol maximal adsorption capacity as the total amount of surface basic groups and carbonyls increases on ACs. He explains this result by the combined effect of a decrease in the mobility of adsorbed molecule with the increase in the content of basic surface groups and a repulsive effect between CO group of the molecule and similar groups attached to the carbon.

On the other hand, under the study conditions, levodopa bears both positive and negative charges, corresponding to the dissociation of COOH function ($pK_a = 2.3$) and protonation of NH_2 function ($pK_a = 8.2$) [33]. This zwitterion has no tendency to migrate in an electric field, thus electrostatic interactions should not occur between the carbon surface and the molecule.

Two mechanisms are thus believed to explain how surface groups influence levodopa adsorption:

- water adsorption (through acidic groups) which clearly penalizes L27,
- donor–acceptor mechanism (through basic groups) which may further explain the difference observed between S23 and C1.

However, despite adsorption on AC has been extensively studied, the extent of contribution of all those possible mechanisms is not yet fully solved. It can be noticed that the highest capacity observed for C1 in the investigated range of concentration corresponds to 2.1 mmol/g, which is of the same order of magnitude as the amount of basic groups measured on this AC.

3.2.2. Isotherm modeling

Table 3 summarizes the results of the nonlinear regression analysis.

From the obtained experimental results, the adsorption process can be well described by Freundlich model for S23 and C1 ACs, with an average relative error of 5%. On the other hand, the three-parameter models give better fitting, but the 95% confidence intervals obtained for K parameter discard those models in case of S23 and question about their relevance for C1.

In the case of L27 carbon, the models with two parameters are not capable to fit adequately the adsorption data; both Redlich–Peterson and Khan models with three parameters describe well the data with acceptable confidence intervals.

AIC_c analysis confirms that Freundlich model should be preferred in the case of S23 carbon, while for both L27 and C1 ACs three-parameter models are more likely: Redlich–Peterson is the best model for L27, but there is no clear evidence in between Redlich–Peterson and Khan models for C1.

It can be mentioned that Toth isotherm equation [34,35], another three-parameter model for heterogeneous surfaces, can also conveniently describe adsorption on L27, while this model was readily discarded for S23 and C1 carbons due to very broad confidence intervals.

Table 3
Model parameters (along with 95% confidence intervals) and goodness of fit. q_{max} is the monolayer capacity; γ, K and a are other model parameters. RSS is the residual sum of squares; AIC_c is the corrected Akaike information criterion and AARE is the average of absolute relative errors.

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
(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

It is known that ACs have strongly heterogeneous surfaces, due to both their pore size distribution and the presence of different functional groups on their surface [36]. It is thus not surprising that idealized models like Jovanovic or Langmuir do not fit well the data for all investigated ACs, although Langmuir equation is still often used to analyse adsorption isotherms on such material. Moreover the presence of several functional groups in the adsorbate molecule has been reported to diversify the interactions with activated carbon sites and thus to increase energy dispersion [37].

4. Conclusions

The adsorption isotherms of levodopa onto three different activated carbons (C1 from casuarine, S23 from coconut shell and L27 from wood) show that C1 has the highest adsorption capacity when compared with L27 and S23. Preliminary studies have been conducted in order to evaluate the differences in the surface chemistry of the three carbons. Adsorption of levodopa appears to be enhanced by the large amount of basic groups present on the surface of C1. This behavior is similar to those reported for phenol and others phenolic compounds. The isotherms are correlated by five models, among which the three-parameter models are found to provide the best fit for the three carbons, with an average relative error between 3% and 5%. However those models lead to broad confidence intervals of parameters in the case of S23 AC. For this carbon, Freundlich model can adequately describe the adsorption process with an average relative error of 5%.

Adsorption on activated carbons appears as a very effective solution to remediate levodopa and could be considered as a tertiary treatment for pharmaceutical wastewaters before discharge.

The problem of adsorbent regeneration, which always limits the application of such process for economical reasons, is also under investigation through the study of sequential adsorption–oxidation processes [38,39].

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