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ADSORPTION OF LEVODOPA FROM AQUEOUS SOLUTION ON GRANULAR ACTIVATED CARBON

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Abstract

Granular activated carbon filtration has been successfully used in wastewater and drinking water treatment plants, for removal of different pollutants and it is the most efficient conventional treatment method for the purification of water contaminated by other pollutants like pesticides. Levodopa is a drug used to treat Parkinson disease, a progressive condition in which the part of the brain responsible for controlling movement stops functioning properly.

In the present study, is reported, for the first time, the adsorption of levodopa from water solution onto activated carbon. The activated carbon was characterized using the low temperature nitrogen adsorption. The equilibrium isotherms at 25 ^{o}C were determined. Five models (Langmuir, Jovanovic, Freundlich, Jovanovic-Freundlich and Radke-Prausnitz) were evaluated to fit the experimental data. The characteristic parameters for each isotherm were calculated and the selection of the most adequate model was performed using the Fisher's test. From the obtained experimental results, the adsorption process can be well described with Jovanovic-Freundlich model ($q=369,21$ mg/g, $a=0,0042$ and $\gamma=0,52$) with an average standard error of estimation of 3,62 %.

Keywords: Levodopa, pharmaceutical waste waters, adsorption isotherms, activated carbon

1. Introduction

The occurrence of pharmaceuticals in the aquatic environment is an emerging concern. Studies in many countries have found more than 80 compounds, including analgesics, antibiotics, antiepileptics, b-blockers and lipid regulators. The presence of drugs in waterways has been established for almost 30 years, but recently concerns have arisen that toxic effects of these compounds may be seen even at very low concentrations (Webb, 2001a,b).

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Pharmaceutically active compounds are produced and used in very large volumes and their use and diversity is increasing every year. Although exact data are rarely available, estimates based on the number of prescriptions suggest that, for example, around 100 tonnes of drugs were prescribed in Germany in 1995 (Ternes, 1998). In the UK in 2000, usage exceeded 10 tonnes per year for all of the top 25 compounds (Jones et al., 2002).

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 (Ternes, 2000).

Research has shown that many pharmaceuticals are not completely removed during wastewater treatment and, as a result, this has led to their occurrence being reported in WTW effluents, rivers and lakes, and more rarely in groundwater (Kolpin et al., 2004, Jones-Lepp et al., 2004, Stackelberg et al., 2004, Bound and Voulvoulis, 2004).

Considering the potential impacts of pharmaceutical products, it is highly important to remove them from wastewater before discharge. The current data suggest that wastewater treatment processes (e.g. activated sludge) have variable performances in removing them. Therefore, it is essential to install additional treatment processes for secondary treatment step. Granular activated carbon (GAC) filtration has been successfully used in wastewater and drinking water treatment plants, to remove different pollutants and it is the most efficient conventional treatment method for the purification of water contaminated by other pollutants like pesticides. Activated carbon is the most efficient adsorbent for organic contaminants due to its high surface area, low specificity and fast adsorption kinetics.

Extensive experimental and modeling studies have been reported to date on the activated carbon adsorption of a broad spectrum of hazardous compounds from aqueous solution (Crittenden et al., 1987; Noll et al., 1992). Yenkie and Natarajan (1991) have reported the adsorption of some organic compounds like phenol, aniline, o-cresol, benzoic - acid, and p-methoxyphenol.

Specifically, the adsorption of different pharmaceuticals has become one of the aims of the researchers in the world. It is possible to find studies for very commons pharmaceuticals like paracetamol (Terzyk, 2000, 2001, 2002; Terzyk and Rychlicki, 2000; Terzyk et al., 2003), aspirine, theophylline (Navarrete Casas, et al., 2006) and 17b-estradiol (Zhang. and Zhou, 2005 and Fukuhara, et al., 2006).

Adsorption mechanisms are so complicated that no simple theory can adequately represent all experimental data. Many expressions have been published to describe the equilibrium relationships between the most commonly used sorbate and adsorbent (activated carbon). Langmuir and Freundlich isotherms are the most common ones and sometimes piecewise equations are used for a selected range of concentration where implementation of only one expression fails badly (Khan et al., 1997).

Levodopa, which molecular structure is represented in figure 1, is one of the several drugs used to treat Parkinson disease. No reports appear in the literature in concern to the treatment of this product. The goals of this study were to determine the adsorption isotherms of levodopa on GAC at 25 ^{o}C and to model obtained data by five models.

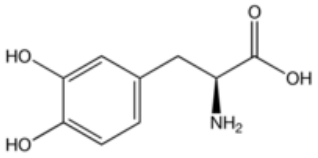

Figure 1. Molecular structure of levodopa

2. Experimental section

Levodopa for synthesis (Sigma-Aldrich) containing more than 99% of pure compound was used for the preparation of the initial solution. Levodopa solutions were prepared from a stock solution and deionised water. The other chemicals and solvents used in chemical analysis were purchased from MERCK

Activated carbon (L27) was supplied by PICA (VEOLIA EAU). Their BET surface area, pore volume, and average pore sizes were measured by nitrogen sorptometry, using an ASAP 2010 version 5.02 analyzer. Specific surface area, S, was calculated from BET plots in the relative pressure range of 0,01-0,1. (Brunauer et al, 1938). Pore volume, V_p, was determined from the amount of nitrogen adsorbed at

relative pressure of 0.985 (Cranston and Inkley, 1957). Mean pore diameter, dp, was calculated from dp $=4V_p/S$, the pore system being assumed to consist of uniform cylindrical nonintersecting capillaries (Gregg and Sing, 1967). Table 1 shows the physical properties of the activated carbon.

Table 1. Physical properties of the activated carbon (S: BET surface area; Vp: total pore volume; dp: average pore diameter; lp: diameter of the particles).

PROPERTIES	L 27
S, m^2g^{-1}	1860
Vp, cm^3/g	1,16
dp, Å	10
lp, mm	0,20-0,40
Microporous volume, cm^3/g	0,7
Mesoporous volume, cm^3/g	0,35

Equilibrium adsorption experiments were carried out using L-27 carbon to evaluate adsorption mechanisms such as the adsorption capacity of the adsorbent. This was done by mixing 100 mL of a solution of levodopa with initial concentration between 0,031g/L and 1,281 g/L with a fixed amount of activated carbon (0,1 g) for 24 hours in a thermostated bath (Polystat 71) at 25 °C. This time was found to be sufficient for the system to reach equilibrium. After mixing, the adsorbent was separated from the adsorbate solution and the concentration of levodopa remaining in solution was measured using an HPLC with a Varian ProStar 310 UV/Vis detector (wave length 278 nm). The equilibrium concentration of levodopa on solid phase was calculated from its initial and final concentrations in aqueous solution. Each experiment was triplicated under identical conditions.

3. Results and discussion

The experimental adsorption data of levodopa on activated carbon L-27 at 25°C are plotted in Figure 2 (experimental data available by request). The average relative error of the measured concentration in the liquid phase was 4.04 %.

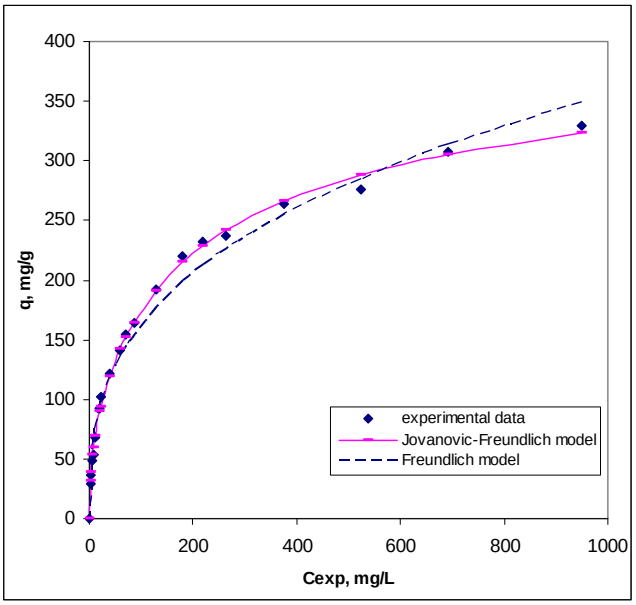

Figure 2. Comparison between experimental adsorption data of levodopa on activated carbon L-27 at 25 °C and values calculated using Jovanovic-Freundlich model.

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Adsorption isotherms are important to understand how adsorbates interact with the support. In this regard, the correlation of adsorption data using either a theoretical or empirical equation is essential for practical propose. Different isotherm models have been used to correlate single component isotherm data. The majority of those models were proposed originally for the treatment of gas mixtures; however, their application to liquid mixtures is supported by theoretical and practical reasons (Jaroniec and Madey, 1988). Among them several types are found: simple isotherm models for homogeneous surfaces without lateral interactions, like the Langmuir model (Langmuir, 1916) and the Jovanovic model (Jovanovic, 1969); isotherm equations for heterogeneous surfaces without lateral interactions, like the the Freundlich model (Freundlich, 1906) and the Jovanovic-Freundlich model (Quiñones and Guiochon, 1996) and empiric isotherm equations, like the Radke-Prausnitz model (Radke and Prausnitz, 1972). The five above mentioned isotherm models (Table 2) were checked in the present study for correlating the equilibrium data.

Table 2. Adsorption isotherm models. q_e the amount of adsorbate adsorbed at equilibrium per unit amount of adsorbent and q_s the monolayer capacity. c_e is the concentration of adsorbate in aqueous phase at equilibrium, ν is the heterogeneity parameter, k, n, and qo other parameters.

Model	Equation
Langmuir	qe=(qs K Ce)/(1+ K Ce)
Jovanovic	qe=qs(1-e^-(KCe))
Freundlich	qe=K (Ce)^γ
Jovanovic-Freundlich	qe=qs(1-e^-(KCe)^γ)
Radke-Prausnitz	qe=qoKCe/(1+K(Ce)^n)

Fitting of the adsorption isotherm models to the experimental data was performed using a non linear regression (Levenberg Marquardt method). The procedure calculates the values of the isotherm parameters which minimize the residual sum of squares (RSS):

$$RSS = \sum_{i=1}^{n} \left(q_{\exp,i} - q_{t,i} \right)^2 \tag{1}$$

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

We used a Fisher's test to compare models that have different numbers of parameters. The selected model exhibited the highest value of the Fisher parameter F_{calc} (Ajnazarova and Kafarov, 1985):

$$F_{calc} = \frac{(n-l)\sum_{i=1}^{n} \left(q_{\exp,i} - \overline{q_{\exp}} \right)^2}{(n-1)\sum_{i=1}^{n} \left(q_{\exp,i} - q_{t,i} \right)^2} \tag{2}$$

Where $\overline{q}_{\exp}$ is the mean value of the vector $q_{\exp,i}$ and l is the number of adjusted parameters of the model.

The standard error of estimation (SEE) was calculated by equation 3

$$SEE = \frac{100}{n} \cdot \sum_{i=1}^{n} \frac{\left| q_{\exp,i} - q_{t,i} \right|}{q_{\exp,i}} \tag{3}$$

Table 3 summarizes the results of the nonlinear regression analysis.

Table 3. Comparison of model correlations. q_s is the monolayer capacity, γ is the heterogeneity parameter. K, n and qo are other parameters. SEE is the average standard error of estimation. F_{cal} is the calculated Fisher parameter.

Model and parameters	Carbon L-27
1- Langmuir	
qs (mg/g)	317,93
K (L/mg)	0,0149
Fcalc	29,39
SEE	17,55
2- Jovanovic	
qs (mg/g)	278,50
K	0,0117
Fcalc	12,13
SEE	24,82
3- Freundlich	
K	35,11
γ	0,3352
Fcalc	49,31
SEE	13,74
4- Jovanovic-Freundlich	
qs (mg/g)	369,21
K	0,0042
γ	0,52
Fcalc	340,98
SEE	3,62
5- Radke-Prausnitz	
qo	72,33
K	0,18
n	0,77
Fcalc	387,64
SEE	4,05

The best fit to the experimental data was obtained for Jovanovic-Freundlich and Radke-Prausnitz models as SEE and F_{calc} values shows. The value of adsorption capacity in Jovanovic-Freundlich model is comparable with those obtained for others products like salicylic acid (351 mg/L) (Otero et al., 2004), o-chlorophenol (380,2), p-chlorophenol (422,1 mg/L) (Aksu and Yener, 2001), 2,4 dichlorophenol (339 mg/L) and 2,4 dinitrophenol (232 mg/L) (Daifullah and Girgis, 1998). Regarding the surface heterogeneity, we can observe that the parameter γ in Jovanovic-Freundlich model is far from the unity, so it can be considered that adsorption of levodopa takes place on heterogeneous surface of L-27 carbon.

4. Conclusions

The present study investigated the adsorption of levodopa onto activated carbon L-27 at 25 °C. The isotherms were correlated by five models among which the Jovanovic-Freundlich and Radke-Prausnitz equations were found to provided the best fit to the experimental data with an average error of estimation of 3,62 % and 4,05 % respectively. The value of adsorption capacity in Jovanovic-Freundlich model is comparable with those obtained for others products and the surface heterogeneity parameter γ suggests that the adsorption of levodopa takes place on heterogeneous surface of L-27 carbon.

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