EFFECTS OF PH AND ACTIVATED CARBON SURFACE CHEMISTRY ON THE ADSORPTION OF CAFFEINE FROM AQUEOUS SOLUTION.

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ABSTRACT: Caffeine adsorption from the aqueous phase was studied using activated carbons vegetal (DD: dendê coco and BB: babassu coco) and an activate carbon commercial (NO: norit® GAC 1240 plus). The functionalized carbons in an inert atmosphere, were denominated DI, BI, NI. Some of the chemical and physical properties of the carbon were studied. Caffeine adsorption was studied in batch experiments at different pH and 23 ^{0}C and adsorption equilibrium data were correlated with the Langmuir and Freundlich equations. Results highlight the importance of pH in caffeine adsorption: the highest removals were obtained for pH 3.0 and decrease for higher pHs. The chance of activated carbon surface increased their adsorption due to a competition effect. The samples are suitable for caffeine removal, although functionalized carbons has advantages, namely, high initial adsorption rate, high adsorption capacity and high removal efficiency, for a large range of pH.

KEYWORDS: Activated carbons, Water hardness, Caffeine, Adsorption kinetics

1. INTRODUCTION

Organic micropollutants as pharmaceutical compounds, endocrine disrupting compounds, pesticides and others, are present in the environment and, due to the increasing concentration detected in recent studies, are arising concern among researchers and regulatory agencies. Most of them are not yet regulated and their impacts on aquatic flora, animals and human life are not quite known. Thus, improved methods of analysis have identified these micropollutants at lower concentrations (μg L^{-1} to ng L^{-1}). Caffeine is considered a chemical marker for surface water pollution due to it is regular consumed over the world. Therefore, it is one of the most abundant xenobiotic in untreated wastewater effluents together with its metabolite paraxanthine and the non-steroidal anti-inflammatory drug acetaminophen (Santiago-Morales et al,. 2012).

In order to remove these emerging contaminants from wastewaters varied physicochemical techniques have been proposed. Adsorption is an efficient and versatile method for the removal of low concentrations of organic pollutants from industrial wastewaters. Among commercial adsorbents, activated carbon is the most commonly used adsorbent. Adsorption on activated carbon has proven successfully in removing caffeine from aqueous solutions, showing a high adsorption capacity (Sotelo et al., 2012).

An alternative is to use low-cost adsorbents with at least reasonable performance to be costly effective (Wang et al., 2008). In this work, two widely produced residues were used for the preparation of low-cost high-value carbon materials: babassu coconut shell and dendê coconut shell. Babassu and dendê are typical Brazilian palm trees that produce vegetal oils used in medicine, food, and even in biodiesel. After the extraction process, the shells are burned to obtain babassu and dendê activated carbons used as adsorbents in organic compound removal, as pesticides, herbicides or insecticides used in
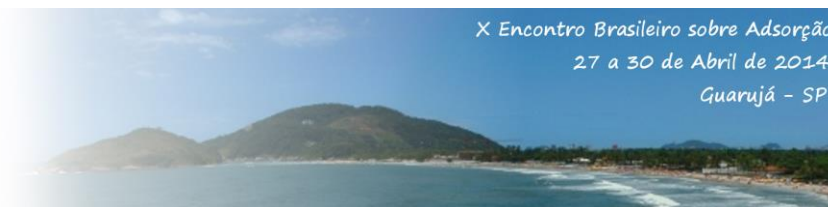
agriculture, heavy metals and pharmaceuticals in wastewater treatment (Karagöz et al., 2008).

The aim of this work was to evaluate the potentialities of two vegetal activated carbons, babassu coco and dendê coco, for the removal of caffeine from aqueous solutions and in the evaluation of the influence of surface chemistry on activated carbon and pH solution on the adsorption process, and model the adsorption process of this pollutant. For comparison purposes one commercial activated carbons commonly used in water treatment are also assayed.

2. EXPERIMENTAL

2.1. Chemicals

Caffeine was purchased from Sigma–Aldrich (Steinheim, Germany), in analytical purity and used in the experiments directly without any further purification. The main characteristics of caffeine are shown in Table 1.

Table 1. Main characteristics of caffeine

Use/Category	Stimulant
CAS/Number	58-08-2
Molecular weigth ($g\ mol^{-1}$)	194.2
[a]Log K_{ow}	0.16
pKa	8.3
Molecular formule	$C_8H_{10}N_4O_2$
Size (Å)	6.9

[a]SRC Physical Properties Database. *Interactive PhysProp Database Demo*, 2011; http://esc.syrres.com/interkow/physdemo.htm
KowWin estimates the log octanol-water partition coefficient, log P, of chemicals using an atom/fragment contribution method developed at SRC.

As shown in this Table 1, caffeine displays basic properties and is present primarily in cationic form at typical drinking water pH values. According to it log Kow values (SRC Physical PropertiesDatabase), this compounds is relatively hydrophilic (as indicated by low values of logKow and moderate solubility).

2.2. Activated carbons

Babassu and dendê activated carbons were gently donated by Carbomafra Ind. and Bahiacarbon Ind.,respectively. Two powdered activated carbons were obtained from coconut shell, babassu coco and dendê coco. A powered activate carbon commercial, Norit® GAC 1240 plus (Norit Américas Ind., Geórgia, EUA), was used as reference.

The commercial activated carbon, Nortit ® GAC 1240 plus, and the activated carbon from coconut shell, babassu coco and dendê coco, were denominated NO, BB, DD, respectively. The fraction used had 80 and 100 mesh, with an average diameter of 0.180 mm.

The procedure to functionalize activated carbon in a tubular reactor, 10 g of carbon activated were placed on a perforated column, which was subsequently placed in an oven programed to heat to 700 ºC for 3 hours under a nitrogen flow rate of 160 mL/min. The activated carbon comercial, Nortit ® GAC 1240 plus, and the activated carbon from coconut shell, babassu coco and dendê coco, functionalized in an inert atmosphere, were denominated NI, BI, DI, respectively.

2.3. Nanotextural and chemical characterization of the carbon samples

The physical characteristics of activated carbons, which include surface area, micropore area, total pore volume, micropore volume and pore size distribution, were assessed by N_2 adsorption in an automatic apparatus model ASAP 2010 from Micromeritics, USA, at 77 K with liquid N_2. Before the experiments, the samples ($\approx$50 mg) were out gassed for 2 h at 300 ^{0}C, under vacuum (10^{-2} Pa). The isotherms were used to calculate the specific surface area and pore volumes. Apparent specific surface area, ABET, was obtained applying the BET equation (in the range $0.05 < p/p_0 < 0.15$) (GREEG & SING, 1982).

The point of zero charge (PZC) of the samples was determined by reverse mass titration, following the method proposed by Noh and Schwarz (NOH & SCHWARZ, 1989). Slurries of (in %) 1, 2, 6 and 10 were prepared by mixing the powdered activated carbon with ultra-pure water in
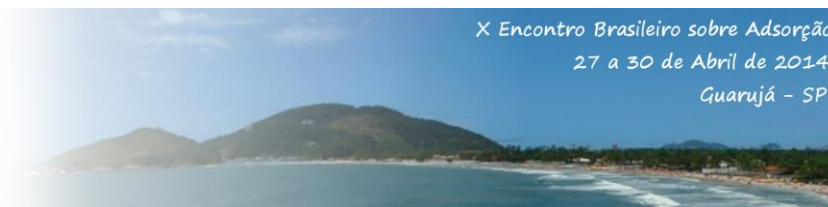
a glass bottle, bubbled and sealed under N_2 (to eliminate CO_2). The pH of the slurry was measured after shaking for, at least, 24 h.

2.4. Caffeine adsorption: kinetics and equilibrium assays

To study the effect of the initial concentration of caffeine (100 mg dm^{-3}) on adsorption kinetics, 20 cm^3 of caffeine solution were mixed with 10 mg of activated carbon in a glass vial, without pH adjustment and with pH adjusted to 3 and 10. The sealed vials were maintained at 23^0C and stirred at 100 rpm. The amount of caffeine was determined, for analysis by UV-VIS spectrophotometer $(\lambda_{máx}= 272\ nm)$. Caffeine uptake was calculated according to the following equation:

$$q_{t=} \frac{(C_0 - C_t).V}{W}$$

where q_t is the amount (mg g^{-1}) of caffeine adsorbed at time t, C_0 is the caffeine initial concentration (mg dm^{-3}), C_t is the caffeine concentration at time t (mg dm^{-3}), V is the volume (dm^3) of the adsorbate solution and W is the weight (g) of dried carbon.

Kinetic experimental points were modeled through pseudo first-order equation (Lagergren, 1898) and pseudo-second order equation (Ho & McKay, 1999).

Equilibrium adsorption studies were made varying the adsorbent doses (4–22 mg), keeping constant the solution volume (20 cm^3), the caffeine concentration (100 mg.dm^{-3}) and the temperature (23 ^0C). The pH of initial caffeine concentration was adjusted to 3, 4.9 and 10 using HCl (1 mol L^{-1}) and NaOH (1 mol L^{-1}) when necessary.

After reaching the equilibrium time, the concentration of caffeine in solution at equilibrium (C_e) was determined and the concentration in the solid phase (q_e) was calculated using Eq. (1). Experimental data were modeled through Langmuir (Langmuir, 1918) and Freundlich (Freundlich, 1926) models.

3. RESULTS AND DISCUSSION

3.1. Characterization of the activated carbons

This work deals with the potential of activated carbon of vegetal origin, from coconut shell, babassu coco and dendê coco, for caffeine removal from aqueous phase. Consequently, for data interpretation purposes the main textural parameters of these vegetal carbons, along with this from the commercial, Norit® GAC 1240 plus, are reported in Table 2.

Table 2. Nanotextural characteristics, and pH_{PZC} of the vegetal carbons activated and commercial adsorbents.

Sample	A_{BET} ($m^2\ g^{-1}$)	V_{TOTAL} ($cm^3\ g^{-1}$)	V_{micro} ($cm^3\ g^{-1}$)	pH_{pcz}
BB	980.53	0.44	0.11	7.4
DD	755.12	0.33	0.07	7.6
NO	1045.23	0.49	0.14	6.6
BI	1011.22	0.46	0.12	9.4
DI	883.96	0.39	0.08	9.2
NI	1125.41	0.56	0.18	8.0

The results from the application of t-plot method reveal all activated carbons, showed high amount of micropore volume, which corresponds to only 75% of the total microporous volume. The activated carbons, NO and NI, have a type I combined with type IV isotherm indicating that they are microporous carbons with an important development of mesoporosity. The functionalization of activated carbon in an inert atmosphere resulted in important changes in surface area and volume pore, compared to equivalent initial carbons.

3.2. Caffeine Adsoption

The pH used was 3, 4.9 and 10, to be consistent with most of the tests for the same concentration. The results are displayed in Figure 1. It is observed that the functionalized activated carbons have a better removal efficiency of caffeine, compared to activated carbons without functionalization.

By analyzing the curves it can be seen that the activated carbons show different kinetic behavior in accordance with the removal efficiency of caffeine, so the activated carbons can be arranged as follows, NI > NO > BI > BB > DI > DD. However, removal efficiency of drugs through

the adsorption process are correlated with pHpzc of activated carbon and the pKa of caffeine The results in Figure 1, show that the pH parameter remarkably influences the removal of caffeine.

The stirring time of 5 h was selected for the equilibrium essays since, according with the results of the kinetic essays; between 2 and 7 h the caffeine uptake was practically the same to all activated carbons.

In all cases, the experimental data were fitted by a pseudo-second order kinetic model (Ho, 2006), with correlation coefficients higher than 0.99, as showed in Table 3. The experimental data were also fitted to the pseudo-first order kinetic model, but the correlations obtained (not shown) were very unfavorable.
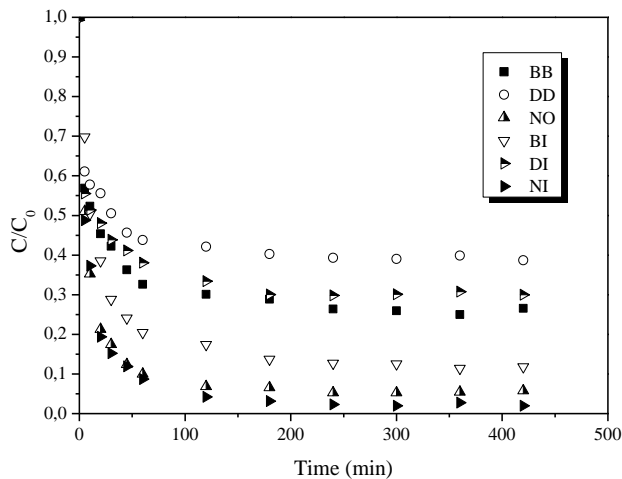

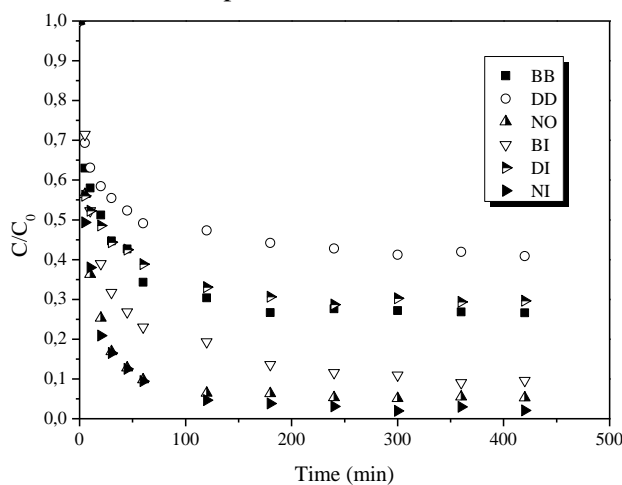**Figure 1a.** Kinetic results of caffeine adsorption for pH 3.0 at 23 ^{0}C.

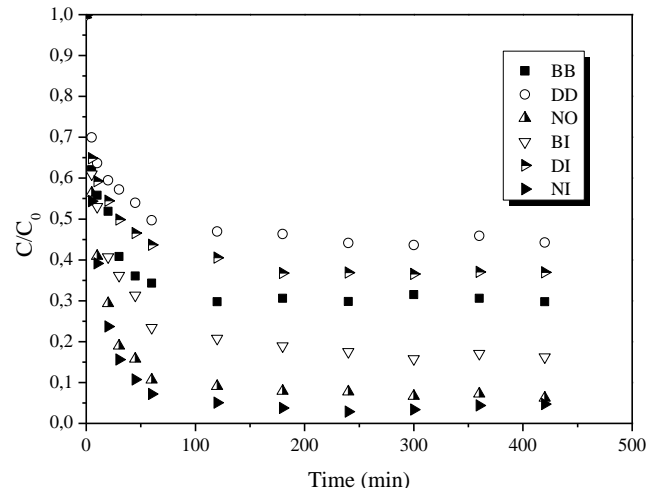Figure 1b. Kinetic results of caffeine adsorption for pH 4.9 at 23 ^{0}C.

Figure 1c. Kinetic results of caffeine adsorption for pH 10.0 at 23 ^{0}C.

According to the result of removal efficiency (r_e) and caffeine uptake (q_e) by these activated carbons, there seems to be some consistence with the microporous volume and surface area.

Research carried out on the adsorption of pharmaceutical compounds onto activated carbon have revealed that the amount of pollutant adsorbed is usually directly proportional to the micropore volume (Mestre *et al.,* 2007; Cabrita *et al.,* 2010; Mestre *et al., 2011*).

For pH 3 and 4.9 (pH < pH$_{PZC}$), activated carbons are positively charged but caffeina, according to the dissociation constant (pKa = 8.3) is adsorbed mostly in the neutral form. For both pH, the adsorption is higher. In these operational conditions, seems that non-electrostatic interactions governed adsorption of caffeine.

Functionalization of the activated carbons, BI, DI and NI, affect the adsorption kinetic. It is possible to observe by the values presented in Table 3, for the pseudo-second order rate constant, k_2, that functionalized activated carbons have a faster adsorption kinetic constant.

The amount of caffeine that remains in solution at equilibrium, $C_{e,calc}$, was determined by the mass balance principle using the $q_{e,calc}$ value obtained from the fitting of the linearized pseudo-second order kinetic equation. The values quoted in Table 3 show that, for all adsorbents, $C_{e,calc}$ slightly decreases with funcionalization of the carbon activated.

Nevertheless, when the initial adsorption rate, h, or half-life time, $t_{1/2}$, are considered the NI sample at pH 3, is the one that presents best
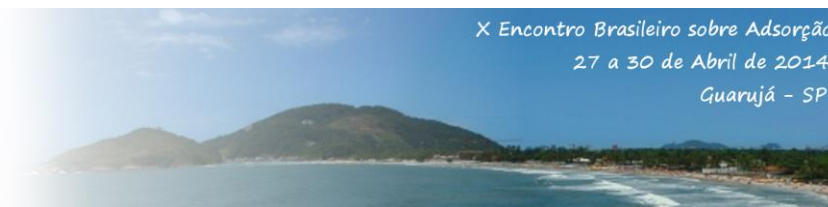
characteristics to remove caffeine from solution. In fact, considering, for instance, the half-life time determined in the essays with $C_0 = 100$ mg mg.L^{-1}, it is obvious that DI sample at pH 3 needs twice the time requested by NI sample for retain half of the caffeine that will be adsorbed at equilibrium. Concerning the pseudo-second order rate constant, k_2, the values at pH 3 and 4.9 presented by DI sample, indicate it removes more caffeine than DD sample (without funcionalized), however these results could be, in part, explained by the fact that that sample present the largest volumes of mesopores (transport pores).

In the essay at pH 3, the funcionalized activated carbons, DI and BI, the initial adsorption rate presented is twice higher than that without funcionalized activated carbons, DD and BB.

On the other hand, for the values of the initial adsorption rate obtained in the essays with BI, DI, NI samples are much more sensitive to initial concentration and always higher than those

found with BB, DD, NO samples. The different behaviour of all adsorbents is most probably a direct consequence of the intrinsic characteristics of their microporous structure. Actually, as already discussed, funcionalized activated carbon sample has a much higher volume of largest micropores than non-funcionalized activated carbon which certainly favours a quicker initial adsorption uptake. The effect of the solution pH was studied for BB and DD. The results showed that this parameter remarkably influences the removal of caffeine. An increase of the pH to BB and DD, above the pH_{PZC} of the adsorbent, 7.4 and 7.6, respectively, leads to the presence of net negative charge on its surface, which revealed to be the worst cases scenario, as the contaminant has the same charge, causing repulsive electrostatic interactions and decreasing the adsorption capacity.

Table 3- Pseudo-second order caffeine adsorption parameters for the studied carbon samples at 23 ^{0}C: k_2 is the pseudo-second order rate constant; h is the initial adsorption rate; $t_{1/2}$ is the half-life time; $q_{e,calc}$ and $C_{e,calc}$, are, respectively, the caffeine uptake and that remaining in solution at equilibrium both calculated by the pseudo-second order kinetic model, and r_e is the removal efficiency.

Samples	k_2 (g mg^{-1} h^{-1})	R^2	h (mg g^{-1} h^{-1})	$t_{1/2}$ (min)	$q_{eq,calc}$ (m g^{-1})	$C_{e,calc}$ (mg dm^{-3})	r_e (%)
pH = 3							
BB	0,00147	0,992	32,89	5,54	149,58	28,34	72,52
DD	0,00142	0,995	20,84	5,81	121,16	42,54	58,74
NO	0,00225	0,998	87,65	2,25	197,38	4,95	95,22
BI	0,00199	0,997	69,75	2,68	187,22	9,88	90,46
DI	0,00193	0,993	36,86	3,75	138,36	33,37	66,56
NI	0,00252	0,999	117,66	1,83	216,08	1,73	98,42
pH = 4.9							
BB	0,00143	0,993	30,97	5,35	147,18	28,53	72,77
DD	0,00139	0,995	19,09	6,13	117,20	44,53	56,82
NO	0,00212	0,995	79,71	2,43	193,90	4,82	95,26
BI	0,00206	0,998	68,30	2,66	182,09	10,14	89,98
DI	0,00183	0,993	32,28	4,00	137,04	33,35	66,26
NI	0,00246	0,999	113,84	1,88	215,13	2,21	97,98
pH = 10							
BB	0,00134	0,993	24,23	5,74	134,48	26,83	69,99
DD	0,00102	0,992	10,60	9,61	101,96	43,09	54,19
NO	0,00178	0,997	55,76	3,17	177,00	6,93	91,73
BI	0,00181	0,995	52,96	3,22	171,06	15,80	84,41
DI	0,00171	0,996	25,80	4,76	122,51	39,26	60,98
NI	0,00190	0,999	69,91	2,74	191,82	5,89	94,21

3.3. Adsoption isotherms

The caffeine adsorption isotherms on the studied activated carbons, at 23ºC and solution pH 3, are presented in Figure 2.

In the case of DD and DI carbons the adsorption isotherms present a less concave curvature; the amount adsorbed steadily increases and the saturation limit at low adsorbent doses is not attained.

By the analysis of the plot depicted for initial concentration of caffeine it is possible to verify that the lower concentration points describes well the first part of the isotherm, which justifies the fact that both models of Freundlich and Langmuir could be applied. The points corresponding to the maximum concentration of caffeine are used to correctly describe the final phase of the adsorption isotherm.

Langmuir and Freundlich parameters, along with the coefficients of determination (R^2) of the linear plots, are presented in Table 4. In all the cases, the experimental data fit better to the Freundlich model since the coefficient of determination of the Freundlich plots ($R^2 \geq 0.992$) are always higher than those obtained for the fitting of the Langmuir model. These results are clearly shown in Figure 2, where the fitting of the two isotherm models are displayed along with the experimental values.
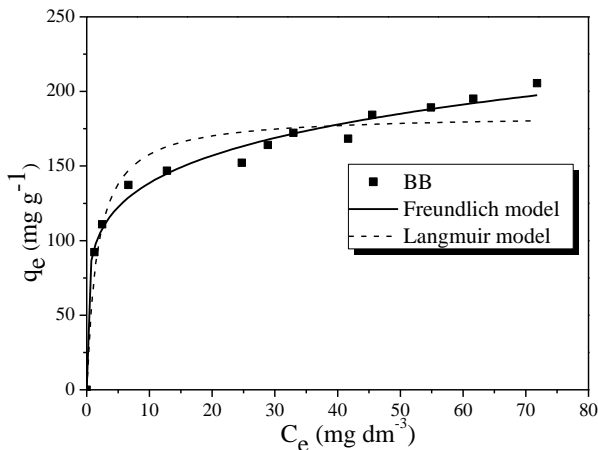

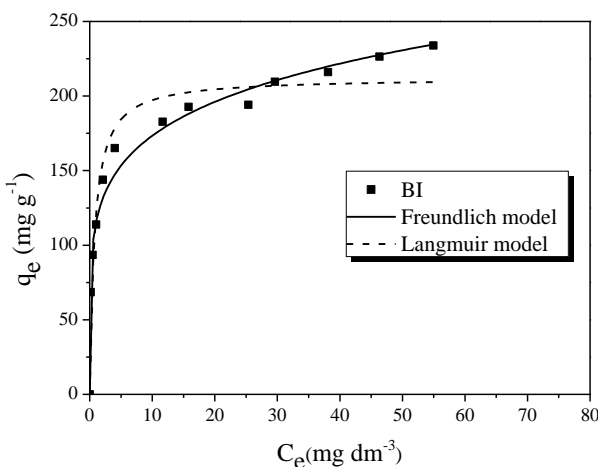**Figure 2.a.** Adsorption isotherms of caffeine onto active carbons, BB, at 23 ºC and pH 3.
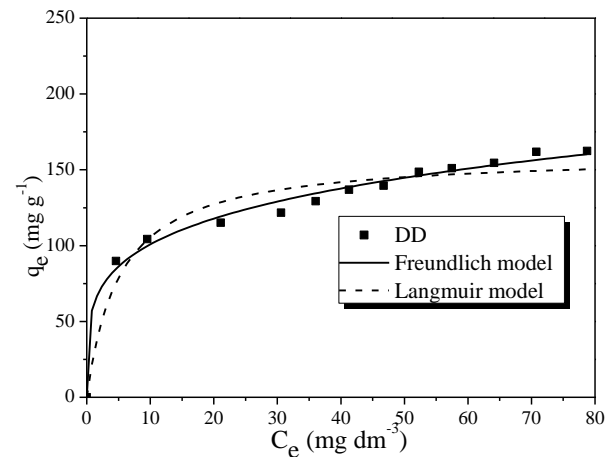

Figure 2.c. Adsorption isotherms of caffeine onto active carbons, DD, at 23 ºC and pH 3.

Figure 2.b. Adsorption isotherms of caffeine onto active carbons, BI, at 23 ºC and pH 3.
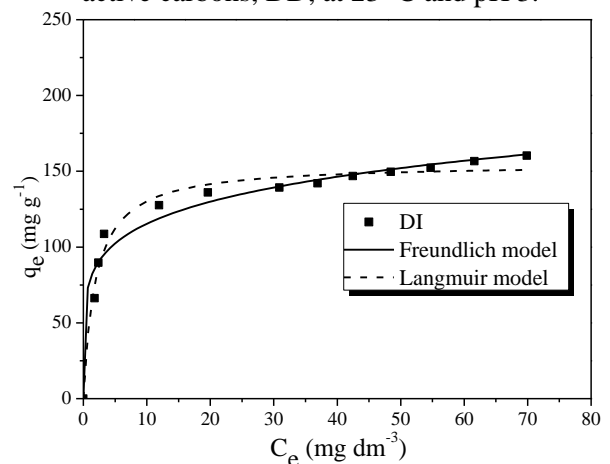

Figure 2.d. Adsorption isotherms of caffeine onto active carbons, DI, at 23 ºC and pH 3.
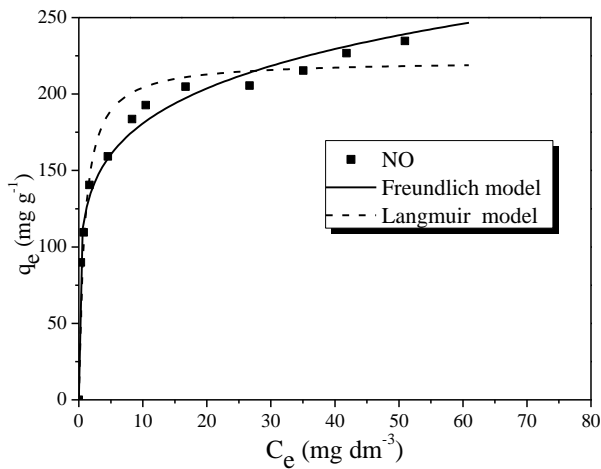
Figure 2.e. Adsorption isotherms of caffeine onto active carbons, NO, at 23 ^{0}C and pH 3.
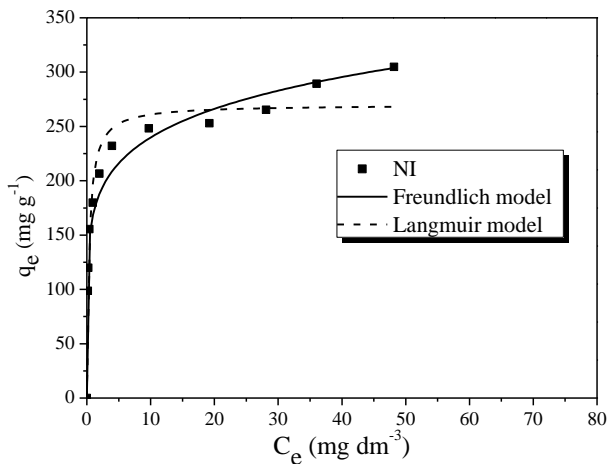

Figure 2.f. Adsorption isotherms of caffeine onto active carbons, NI, at 23 ^{0}C and pH 3.

In Table 4 the results of the non-linear chi-square test analysis, χ^2, are also presented. In a recent study Ho (2004) discussed the advantages of using this analysis to compare the fitting of experimental data to isotherm models. χ^2 is determined using the following equation:

$$\chi 2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}}$$

where q_e is the experimental equilibrium uptake and $q_{e,m}$ is the equilibrium uptake calculated from the model. From this equation it is clear that if the values calculated from the model are similar to experimental data, χ^2 should be a small number and vice versa. The χ^2 values displayed in Table 4 corroborate Ho's conclusions since from χ^2 values the worst fitting of the Langmuir model is much

clear than what is observed when R^2 values are considered. On the other hand, in what concerns Freundlich model the better fitting for the isotherms obtained with BI, DI and NI samples are highlight when χ^2 values are considered. .

The adsorption capacities, q_m, increase according to the following order: DD < DI < BB < BI < NO < NI. This trend has to be linked to both porous and chemical features of the adsorbents. However, it appears that the uptake is related to the apparent surface area since, for instance, the carbon with the largest A_{BET} value, NI, has the higher caffeine uptake.

Table 4 - Fitting parameters to the Langmuir and Freundlich models, chi-square test analysis, χ^2.

	Freundlich model			
Sample	1/n	K_F	R^2	χ^2
BB	0.179	91.73	0.997	8.56
BI	0.177	115.22	0.992	4.29
DD	0.224	60.08	0.998	9.49
DI	0.172	77.65	0.998	5.91
NO	0.172	121.70	0.995	5.77
NI	0.150	169.57	0.998	3.21
	Langmuir model			
Sample	q_m	b	R^2	χ^2
BB	186.90	0.451	0.952	14.69
BI	212.39	1.294	0.935	11.20
DD	159.33	0.202	0.899	13.89
DI	205.02	0.511	0.964	8.97
NO	223.02	1.057	0.951	15.72
NI	270.20	2.83	0.924	8.85

Nevertheless, we have found that the carbon with the lowest narrow micropore volume, DD, does not outperforms caffeine retention on the rest of the adsorbents. In fact, a closer look to the isotherms showed correlation between the loading capacities and the narrow microporosity of the carbons evaluated from N_2 adsorption data, as showed in Table 1.

In fact, one can always admit that this difference is a consequence of the packing of caffeine molecules in the porous structure that, most probably is not completely filled with the
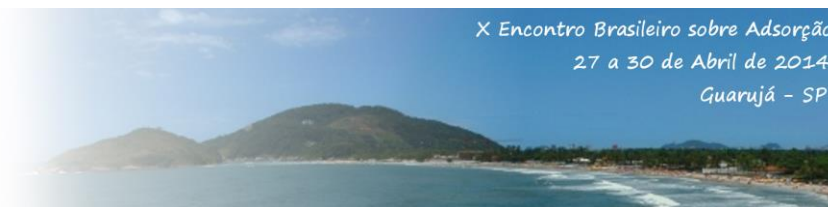
adsorbate species. Nevertheless, considering the nature of the surface chemistry groups of all activated carbons, another justification for this result can be considered.

As it was already mentioned, the Langmuir constant, b, is a measure of the adsorption affinity or heterogeneity of the surface. So, according to the b values quoted in Table 4, the BI, DI, NI sample has higher adsorption affinity to the caffeine than the BB, DD, NO sample.

So, considering the values of V_{micro} (Table 2) it is evident that the sample with the small mean micropore width (BI, DI, NI) are the one that presents high Freundlich constant values and consequently high adsorption affinity. The 1/n values show that BI, DI and NI samples has higher adsorption affinity than the BB, DD and NO samples. So, it seems that both models are consistent in indicating that the adsorption affinity of the activated carbons is different, being highest for the functionalized activated carbon sample.

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