Effect of Solution pH on the Removal of Paracetamol by Activated Carbon of Dende Coconut Mesocarp

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Activated carbon of dende coconut mesocarp was used to investigate the removal of paracetamol from water by adsorption. The results indicated that the retention of paracetamol was favored in activated carbon with neutral surface properties. The textural features and presence of a transport pores network contributed to ensuring the accessibility to the inner porosity, and the microporosity must be large enough to accommodate the paracetamol molecule. Chemisorption and mainly physisorption are important in the paracetamol removal. Pseudo-second order equation and Langmuir model were chosen to best present the experimental data. The adsorption process was non-spontaneous and endothermic with increase in system disorder.

Key words
paracetamol, adsorption, activated carbon, dende coconut

Introduction

The production of pharmaceuticals has increased rapidly in the last decades, providing better health quality for humans and animals. Upon their use, large amounts of pharmaceuticals are discharged into the water bodies, and are thus detected in wastewater and surface water at ng L^{-1} to μg L^{-1} levels[1,2]. Conventional wastewater treatments for pharmaceuticals are ineffective in eliminating and/or degrading most of these compounds. Therefore, residual quantities remain in the treated water, and have been found to accumulate in drinking water[3,4]. Particularly, paracetamol is one of the pharmaceuticals of common use worldwide due to its effectiveness in the relief of pain and fever. Unfortunately, its presence in recycled water has already been detected[5].

In this context, adsorption may improve wastewater treatment. As adsorbents, activated carbons from biomass residues have been widely studied. Among these residues stand out cork powder[6], peach stones, and PET bottles[7], coconut endocarp and palm endocarp[8], olive stone[9], tobacco residue[10] sisal waste[11], mangosteen peel[12], coconut mesocarp[13], oil palm empty fruit bunch, bamboo stem, coconut shells[14]. Indeed, researchers have been seeking the best adsorbent to solve a local problem through the available natural disposals.

Therefore, in this work, the activated carbon from dende coconut residue was used to remove paracetamol. Dende is a typical Brazilian palm tree that produces oil, which is applied in medicine, food industry, and even as biodiesel. The dende activated carbon was obtained by burning mesocarp fibers and dende peels[15].

Adsorption of paracetamol on carbon has been widely studied by Terzyk[16], Villaescusa[17], Mestre[11] and Ribeiro[18]. Nevertheless, biosorbents based on industrial and agricultural wastes to remove organic compounds are scarely investigated.

In order to fulfill this lack of information, this paper presents results related to the influence of temperature and pH in the adsorption process. Kinetics, equilibrium data, as well as thermodynamics are reported.

Materials and methods

Adsorbents

The activated carbon of dende coconut mesocarp was kindly supplied by Bahiacarbon Inc. (Bahia, Brazil).

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The samples were previously washed with hot deionized water (50 °C), dried in an incubator for 24 h at 60 °C, ground and sieved with average diameter of 0.180 mm (70–100 mesh ASTM). No previous chemical or physical treatment was done.

Nanotextural and chemical characterization of the carbon samples

The activated carbon was characterized by N_2 adsorption in ASAP 2000 Micromeritics equipment at –196 ºC and 0 ºC with liquid N_2.

Prior to the experiments, the samples were outgassed for 2 h at 300 ºC, under vacuum (10^{-2} Pa). The isotherms were used to calculate the specific surface area (S_{BET}), total pore volume, micropore volume and pore size distribution. Apparent specific surface area was assessed applying the BET equation (in the range $0.05 < P/P_0 < 0.30$). The point of zero charge ($\mathrm{pH_{PZC}}$) was estimated using the mass titration procedure[18].

Adsorbate

Paracetamol or acetaminophen (*N*-(4-hydroxyphenyl)ethanamide), the common name of *N*-acetil-*p*-aminophenol, was bought by Sigma-Aldrich (purity 98 %). All paracetamol solutions contained 10 % v/v of methanol and concentration of 50 mg dm^{-3}. They were prepared with ultra-pure water obtained from Milli-Q water purification systems. The pH solutions of paracetamol were adjusted to 2, $\mathrm{pH_{PZC}}$ and 11 adding 0.1 mol dm^{-3} of HCl or NaOH. A volume of 20 cm^3 of the paracetamol solutions was used in all adsorption studies.

Kinetic of adsorption

Kinetic adsorption studies were carried out in finite bath (Dubnoff, Nova Ética) systems at 25 ºC and 150 rpm, where the paracetamol solution was mixed with 10 mg of activated carbon in glass vials. Time-recording started when the stirring began, and samples were collected between 5 minutes and 8 hours. After filtration, paracetamol concentration was determined for analysis by UV-VIS spectrophotometry technique using Hach DR 5000 equipment ($\lambda_{\max}$ = 240 nm). Paracetamol removal was calculated according to the following equation:

$$q_t = \frac{(\gamma_0 - \gamma)}{m} V \tag{1}$$

where q_t is the amount (mg g^{-1}) of paracetamol adsorbed at time t, γ_0 is the paracetamol initial concentration (mg dm^{-3}), γ is the paracetamol concentration at time t (mg dm^{-3}), V is the volume (dm^3) of the adsorbate solution, and m is the mass (g) of dried activated carbon of dende coconut mesocarp.

The mechanism of adsorption and kinetic parameters sorption data were analyzed using pseudo-first-order[20] and pseudo-second order models[21].

The pseudo-first-order rate equation of Lagergren based on solid capacity is expressed as follows:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_1(q_e - q_t) \tag{2}$$

where k_1 is the constant rate of pseudo-first-order adsorption (min^{-1}), q_e (mg g^{-1}) is the amount of paracetamol at equilibrium, and q_t (mg g^{-1}) is the amount of paracetamol at time t (min).

Integration of Eq. (2) for the initial conditions $t = 0$ and $q_t = 0$ gives:

$$q_t = q_e(1 - e^{-k_1 t}) \tag{3}$$

The pseudo-second-order kinetic model equation is expressed as follows:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_2(q_e - q_t)^2 \tag{4}$$

where k_2 is the constant rate of pseudo-second-order adsorption (g mg^{-1} min^{-1}), q_e (mg g^{-1}) is the amount of paracetamol at equilibrium, and q_t (mg g^{-1}) is the amount of paracetamol at time t (min).

Integration of Eq. (4) for the initial conditions $t = 0$ and $q_t = 0$ gives:

$$q_t = \frac{q_e^2 k_2 t}{1 + k_2 q_e t} \tag{5}$$

Equilibrium modeling

Equilibrium adsorption studies were carried out varying the adsorbent doses (0.07–60 mg), keeping constant the solution volume (20 cm^3), and the temperature (25 ºC).

Adsorption isotherms are the equilibrium relationships between the concentrations of the adsorbed paracetamol and the paracetamol ion in the solution at a given temperature. Langmuir and Freundlich isotherm models were used to investigate the adsorption equilibrium between the paracetamol solution and the activated carbon phase.

The Langmuir adsorption isotherm equation, expressed as follows, requires for its applicability a mono-layered coverage on the surface of adsorbent[22]:

$$q_e = \frac{q_{\max} k_L \gamma_e}{1 + k_L \gamma_e} \tag{6}$$

where q_e, k_L, $q_{\max}$ and γ_e are the paracetamol uptake at equilibrium (mg g^{-1}), the Langmuir constant (dm^3 mg^{-1}), the monolayer adsorption capacity (mg g^{-1}) and the solution concentration at equilibrium (mg dm^{-3}), respectively. The Freundlich equation is applicable for multi-component adsorption. The Freundlich isotherm is expressed by[23]:

$$q_e = k_F \gamma_e^{1/n} \tag{7}$$

where k_F is the Freundlich constant (mg$^{1-1/n}$ (dm^3)$^{1/n}$ g^{-1}), and n is the Freundlich exponent. The Freundlich equation was successfully used to fit the experimental data for many fluid–solid systems, but one of the main drawback of this equation is that it does not tend to a limiting value when the equilibrium concentration increases.

Thermodynamic parameters

It is well known that thermodynamic parameters can evaluate the orientation and feasibility of the physicochemical adsorptive reaction. The three thermodynamic parameters considered were standard enthalpy ($\Delta H°$), standard free energy ($\Delta G°$), and standard entropy ($\Delta S°$). The value of $\Delta H°$ and $\Delta S°$ was obtained from the following equation:

$$\ln K = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{8}$$

where K is called the adsorption affinity and corresponds to the ratio of q_e, related to the amount adsorbed per unit mass (mg g^{-1}), and γ_e, the equilibrium concentration (mg dm^{-3}) of the solute ($K = q_e/\gamma_e$), R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute solution temperature (K). The values of $\Delta H°$ and $\Delta S°$ were determined from the slope and the intercept of the linear plot of ln K versus $1/T$, and from these values Gibbs free energy ($\Delta G°$) was calculated as follows:

$$\Delta G° = \Delta H° - T\Delta S° \tag{9}$$

The effect of temperature on adsorption was studied at 298, 308 and 318 ± 1 K, by considering samples of activated carbon (0.07–60 mg) added in paracetamol solution and constantly stirred until equilibrium time.

Results and discussion

Characterization of the adsorbent

The nitrogen adsorption-desorption isotherm is presented in Fig. 1. The activated carbon of dende coconut mesocarp was a typical microporous–mesoporous material (type I in the IUPAC classification) with a hysteresis loop (H4 types) in the desorption branch at relative pressures above 0.5. The adsorption–desorption hysteresis on activated carbon isotherm showed clearly that liquid nitrogen was condensed in slit-shaped mesopores[24].

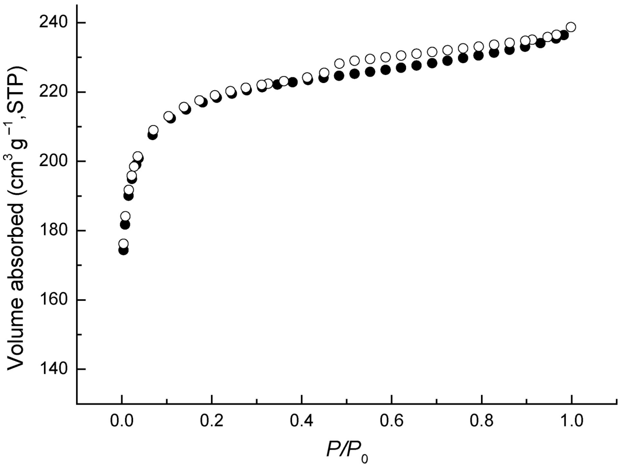

Fig. 1 – N_2 *adsorption–desorption isotherms at 77 K of the dende (●) adsorption and (○) desorption*

The S_{BET} surface area of activated carbon was 672 m^2 g^{-1}. Total pore volume obtained was 0.369 cm^3 g^{-1}, 0.287 cm^3 g^{-1} related to micropores and 0.082 cm^3 g^{-1} related to mesopores. Fig. 2 depicts the pore diameter distribution. The average pore diameter of 34.5 Å indicated that the activated carbon was in the micropores (region < 20 Å) and mesopores (region between 20 to 500 Å). Regarding the surface chemistry, the value of pH$_{PZC}$ revealed that the activated carbon presented predominantly neutral nature with value of 6.5.

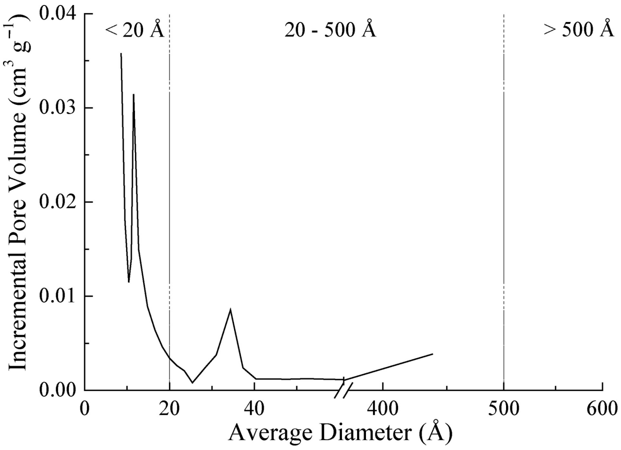

Fig. 2 – *Pore diameter distribution curves, based on the BJH method for dende activated carbon*

Paracetamol adsorption

Kinetic studies and the effect of solution pH

This study was carried out with the control of pH and temperature, as reported by Fontecha-Cámara[25]. The study of adsorption from aqueous solutions requires at least the control of these

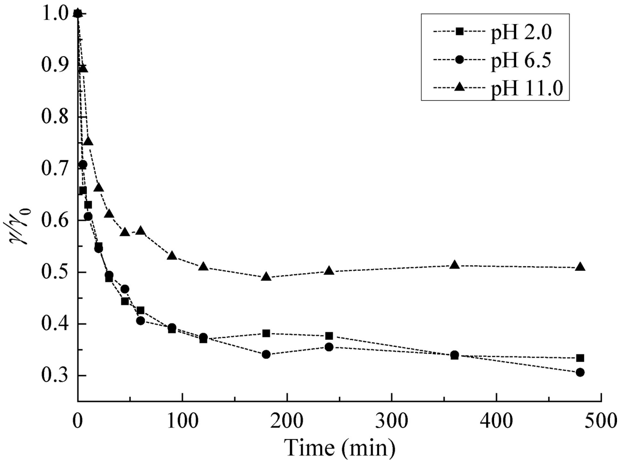

Fig. 3 – *Kinetic results of paracetamol adsorption at 25 °C to pH 2.0, 6.5 and 11.0*

parameters, with no addition of salts. The adsorption that occurs in a solid–liquid is generally more complex than that verified in a solid–gas, as water is a reactive solvent, present in various forms (H_2O, OH^- and H^+). Concentration of each species depends on the pH[5].

Kinetic results are displayed in Fig. 3.

Paracetamol removal efficiency was very similar for pH values of 2.0 and 6.5. Concentration decreases rapidly at pH 6.5 and 20 up to 120 min. Then after such time it was assumed that this system reached equilibrium.

Differences between kinetic curves of pH 2 and 6.5 compared to the one obtained for pH 11 are due to the pH influence in the ionization state of weak electrolyte of paracetamol (p*K*a~9) and the charges that may appear in the carbon surface. At pH 11, paracetamol molecule was repealed by the negatively charged carbon surface[26,27]. At pH_{PZC} and pH 2, the neutral paracetamol molecules were adsorbed by the equally neutral and positively charged adsorbent surface.

The amount of pharmaceutical compounds adsorbed onto activated carbon is usually directly proportional to the micropore volume[6,26,27]. Therefore, the promising results obtained at pH 6.5 and 2 may be a consequence of the significant contribution of the predominant microporous adsorbent and its surface charge. Probably, the carbonyl group of paracetamol induced some chemisorption, although physisorption should have higher contribution mainly in the micropores, in which the molecule can be better retained. In basic solutions with pH > p*K*a, the amount retained represented a drastic decrease due to the anionic charges involved.

The adjusted parameters of adsorption kinetics at pH 2.0, 6.5 and 11.0 (Table 1) were calculated from the non-linear regressions of the integrated Eqs. (2)–(5).

The best fitting of adsorption kinetics at pH 6.5 ($R^2 = 0.988$) was obtained for the pseudo-second-order model. The maximum amount of paracetamol experimentally retained in equilibrium was 65.57 mg g^{-1} for pH 2.0, 64.85 mg g^{-1} for pH 6.5, and 44.12 mg g^{-1} for pH 11.0 similar to the ones predicted by the pseudo-second order model. Moreover, it was seen that adsorption decreases in basic solutions. The pseudo-second-order rate constant k_2 obtained at pH 11.0 (0.0016 g mg^{-1} h^{-1}) was lower than at pH 6.5 (0.0018 g mg^{-1} h^{-1}), indicating that the paracetamol adsorption at pH 11.0 required a higher amount of activated carbon than at pH 6.5 to reach the same adsorption efficiency.

Adsorption isotherms

Fig. 4 illustrates the paracetamol adsorption isotherms. The isotherm shape may be classified as L type[28], characteristic of a steep initial rise and a concave curvature at low equilibrium concentrations typical by a plateau or saturation limit. This is characteristic of systems where the adsorbate presents high affinity towards the adsorbent, and therefore indicates no strong competition of the solvent for the active sites of adsorption.

Table 1 – *Kinetic modeling of paracetamol adsorption*

Kinetic model	Parameters	pH = 2.0	pH = 6.5	pH = 11.0
Pseudo-first-order	q_e (mg g^{-1})	59.11±1.892	58.31±1.756	43.07±1.142
	k_1 (h^{-1})	0.092±0.016	0.081±0.013	0.055±0.005
	R^2	0.911	0.928	0.979
Pseudo-second-order	q_e (mg g^{-1})	63.11±1.244	62.91±0.929	46.81±0.804
	k_2 (g mg $^{-1}$ h^{-1})	$0.0020\pm3.3\cdot10^{-4}$	$0.0018\pm1.9\cdot10^{-4}$	$0.0016\pm1.7\cdot10^{-4}$
	R^2	0.976	0.988	0.978

k_1 is the pseudo-first-order rate constant; k_2 is the pseudo-second-order rate constant; q_e is the amount of paracetamol at equilibrium.

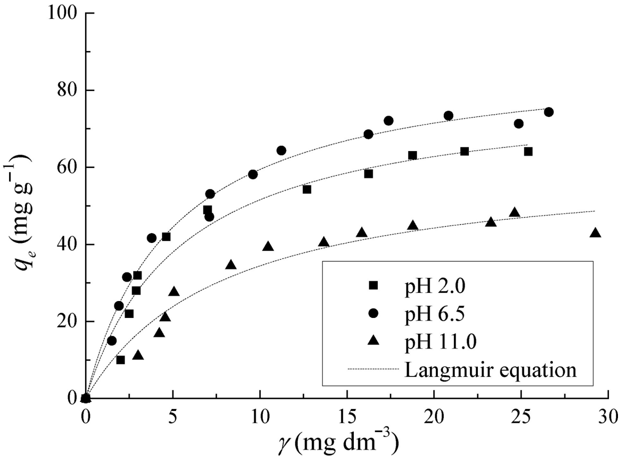

Fig. 4 – *Experimental adsorption isotherms of paracetamol onto activated carbon at 25 °C and solution pH 2.0, 6.5 and 11.0 fitted to Langmuir model*

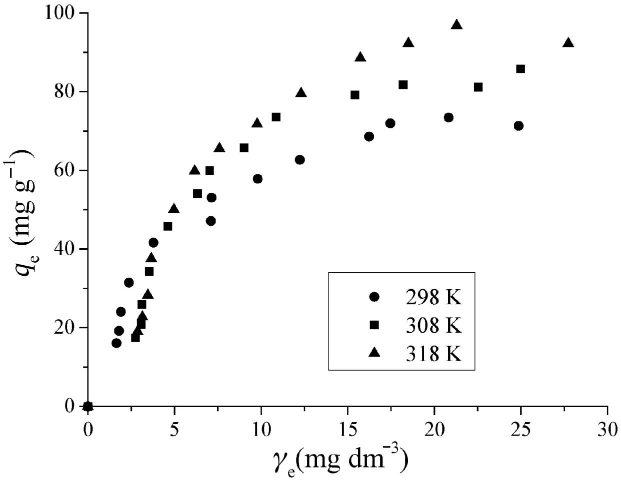

Fig. 5 – *Experimental adsorption isotherms of paracetamol onto activated carbon at 298, 308 and 318 K*

The experimental adsorption isotherms were fitted to the classic Langmuir[22] and Freundlich models[23] (equations (6) – (7)).

The maximum experimental retention of paracetamol (q_t) was 64.75 mg g^{-1} for pH 2.0, 74.31 mg g^{-1} for pH 6.5, and 42.75 mg g^{-1} for pH 11.0. It is possible to verify (Table 2) that Langmuir adjustment obtained the best fitting with higher R^2 and lower parameter deviation. Then, such model was chosen as one that best represents experimental data. Comparison of maximum experimental retention of paracetamol and the $q_{\max}$ from Langmuir verified that the maximum amount was not experimentally reached. It can be noted that the highest removal was obtained for pH 2.0 and 6.5, which is in agreement with the kinetic data and can be explained through p*K*a and surface pH. Moreover, samples with pH 2.0 and 6.5 presented the highest adsorption affinity (k_L values) to paracetamol molecules, according to data quoted in Table 2.

Isotherms at 298 K, 308 K and 318 K were obtained in neutral (pH 6.5). As most wastewaters have this characteristic. Figure 5 shows such experimental data where it can be seen that increase temperatures provide higher paracetamol removal. This is in accordance with the fact that chemisorption played an important role in the global adsorption.

Adsorption thermodynamics

The isotherms at different temperatures were used to estimate the adsorption parameters.

Values of ΔH^o, ΔS^o and ΔG^o are shown in Table 3. The ΔG^o values for all temperatures were positive, which reflected the non-spontaneous nature of the adsorption processes. The positive ΔH^o value indicated that the adsorption process was endothermic in nature. Possibly an increase in temperature is needed for better accommodation of paracetamol molecules previously attracted by the superficial positive charge in the micropores. The

Table 3 – *Thermodynamic parameters for the adsorption of activated carbon of dende coconut mesocarp*

T (K)	$\Delta G°$ (kJ mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (kJ mol^{-1})	R^2
298	4.434	16.666	71	0.945
308	5.366			
318	5.845			

Table 2 – *Fitting parameters of the equilibrium adsorption isotherms to the Langmuir and Freundlich models*

Isotherms	Parameters	pH = 2.0	pH = 6.5	pH = 11.0
Langmuir equation	$q_{\max}$ (mg g^{-1})	80.620±1.599	90.813±3.073	62.911±5.872
	k_L (dm^3 mg^{-1})	0.280±0.026	0.187±0.019	0.117±0.029
	R^2	0.980	0.984	0.925
Freundlich equation	k_F (mg$^{1-1/n}$ (dm^3)$^{1/n}$ g^{-1})	25.843±1.937	21.398±2.209	12.212±2.388
	$1/n$	0.281±0.349	0.404±0.235	0.422±0.393
	R^2	0.948	0.944	0.879

positive value of ΔS° indicates an increase in the degree of freedom (or disorder) of the adsorbed species[29] related to the attraction and diffusion into the adsorbent.

Conclusions

The potentialities of activated carbon, obtained from dende coconut mesocarp residues, for the removal of paracetamol was investigated. Acid or neutral pH solutions promoted paracetamol adsorption due to the electrostatic interaction between adsorbate/adsorbent. Physisorption and mainly chemisorption are important in paracetamol removal. Pseudo-second-order equation and Langmuir model were chosen to best present the experimental data. The adsorption process was non-spontaneous and endothermic with increase in system disorder.

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