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PFOA ADSORPTION KINETICS ON NATIONAL ACTIVATED CARBON: PRELIMINARY STUDY

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Abstract: The present work exposes the problem of water contamination by a class of anthropogenic chemical substances known as per- and polyfluoroalkyl substances (PFAS) that have been widely used in various industrial processes since the 1940s. The use of PFAS in the production of textiles, Non-stick coatings, stain-resistant materials and firefighting foam result in significant environmental contamination, especially in areas where these products are manufactured and used due to the ability of PFAS to bioaccumulate in organisms, leading to toxic effects. Although conventional water treatment techniques can remove many contaminants, PFAS are not effectively removed by these methods and even the use of advanced oxidative processes has been shown to be ineffective at removing PFAS from water. Faced with this challenge, research has focused on the use of powdered activated carbon (PAC), a common adsorbent for removing contaminants in water. The study describes experiments conducted on a bench scale at ``Universidade de Brasília`` (UnB) using commercial pulverized activated carbon produced from the endocarp of the babassu coconut (CAP Babassu) aiming to evaluate the adsorption kinetics of perfluorooctanoic acid (PFOA) on carbon in a matrix of ultrapure water given that there are few studies on the removal of PFAS in Brazil. The initial characterization of the coal was carried out using thermogravimetric analysis and PCZ pH test. Quantification of the analyte was carried out using a Shimadzu Total Organic Carbon analyzer. The study evaluated the adsorption kinetics of perfluorooctanoic acid (PFOA) using pseudo-first and pseudo-second order models. The results were analyzed using the linear regression technique and plotted on graphs representing the model equations. In the end, activated carbon from babassu coconut endocarp proved to be a potential adsorbent for use in the removal of PFOA (qe=120 mg PFOA/g CAP Babassu), following a pseudo-second order kinetic model, suggesting the predominance of chemical adsorption and coexisting with physical adsorption.

Keywords: PFAS, PFOA, Kinetics, Adsorption, Activated carbon.

INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) make up a class of anthropogenic – or man-made – chemicals and have been used for a wide variety of industrial processes since their development in the 1940s.

The use of PFAS, mainly perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), in the manufacture of textiles, non-stick coatings and stain-resistant materials, among other applications, has resulted in the presence of these substances in all environmental compartments, contaminating water supply in areas where these products are manufactured and used (US Environmental Protection Agency, 2022a).

In addition to these commercial uses, PFAS, mainly perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), have been identified as excellent compounds in the composition of high-intensity fire suppressants due to their intrinsic chemical characteristics, leading foam manufacturers firefighting agent aqueous film former to include PFAS in its mixtures.

The bioaccumulation of PFAS in organisms is concerning due to evidence of toxic effects involving these chemicals. Toxicological data for such compounds has existed for some time, with studies dating back to the 1980s, and after more than 70 years of use in various industries, it is becoming increasingly clear that some PFAS are readily absorbed into human tissues in a manner similar to other mammals studied (Whittaker and Heine, 2018).

Although drinking water treatment plants are capable of removing many organisms, particles, and chemical compounds from drinking water, PFAS are not effectively removed through conventional water treatment techniques, including coagulation, flocculation, and sedimentation (Quiñones and Snyder, 2009). The use of contemporary water treatment technologies, namely advanced oxidative processes such as ultraviolet radiation (UV), ozone (O3), hydrogen peroxide (H2O2), among others, also presents low efficiency in removing PFAS (Appleman et al., 2014).

The low reactivity of PFAS, which makes them so useful in countless applications, is also responsible for making them highly persistent in the environment. Thus, this attribute has made it particularly difficult for public water systems to eliminate PFAS at the level of the recently instituted Health Advisory Level (HAL) imposed by the United States Environmental Protection Agency (USEPA).

For example, recently in June 2022, the USEPA made public that the Health Advisory Level (HAL) for drinking water for PFOA and PFOS are 0.004 and 0.02 ng/L, respectively. Additionally, the USEPA signaled that, still in 2022, it would establish the Maximum Contaminant Level Goal (MCLG) in water for human consumption for both PFOA and PFOS, indicating that the value to be adopted would be less than 4 ng/L (US Environmental Protection Agency, 2022b).

The issues of low reactivity and new guidelines present an obvious problem for public water treatment systems, regulators, or any party concerned about the contamination of drinking water supplies by these compounds.

Research has been carried out focusing on the use of powdered activated carbon (PAC), which is a common adsorbent used to treat a wide variety of contaminants in water, which, due to its large surface area, lends itself to accumulating large amounts of contaminants (Herrera and Alvarez, 2008; Rattanaoudom et al., 2012).

Given the above, and the lack of studies related to the removal of PFAS carried out in Brazil, the present work aims to evaluate the adsorption kinetics of PFOA in ultrapure water by commercial activated carbon produced from coconut endocarp of babassu.

MATERIALS AND METHODS

As this is a recent topic in Brazil, the present study refers to preliminary experiments carried out on a bench scale at ``Universidade de Brasília`` (UnB).

A commercial pulverized activated carbon produced from babassu coconut endocarp (CAP Babassu) was purchased. This charcoal was then washed in deionized water, filtered through 0.45um cellulose acetate and dried in an oven for 12h at $100^{\circ}C$. The activated carbon stock solution was prepared using 3g of carbon in 60mL of ultrapure water, the mixture being sonicated for 5 minutes and placed under vacuum for 12h, aiming for complete hydration of the material.

The initial characterization of the coal was carried out using thermogravimetric analysis in a nitrogen atmosphere (equipment: Shimadzu DTG-60, 50mL $N.min^{-1}$, 25 a $900^{\circ}C$, $10^{\circ}C.min^{-1}$) and the pHPCZ test, carried out using the 11-point pH balance method.

The adsorbate used was PFOA, prepared from 1g of the standard (Merck, 95% purity) in 1L of ultrapure water ($1mg.mL^{-1}$). To evaluate the concentration of adsorbate present in the samples, a Total Organic Carbon analyzer (Shimadzu TOC-L) was used, and a calibration curve was constructed to quantify the analyte. The curve was prepared following the methodology described in the equipment manual, with carbon standards being prepared for 6 calibration points, thus meeting a

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measurement range of 2 to 64 mg C.L-1, which corresponds to a concentration range of 8.6 to 138 mg PFOA.L-1. Therefore, the procedure for quantification is representative since the matrix used was ultrapure water.

The kinetic test was conducted in a 2L Erlenmeyer flask containing: 390mL of ultrapure water; 100mL of PFOA stock solution (1mg.mL-1); and 10mL of activated charcoal stock suspension (50mg.mL-1), resulting in initial concentrations of 200mg.L-1 of PFOA and 1000mg.L-1 of charcoal. The pH of the solution was adjusted to 6.5 with 0.1M NaOH.

The test was carried out in a climate-controlled orbital shaker model SI-600R (Lab Companion), maintained at 200 rpm and 25ºC. Throughout the test, 8 aliquots of 25mL were removed at times: 0; 1; 6; 8; 32; 64; 256 and 512 minutes, which were immediately filtered through a 0.45μm pore cellulose acetate filter and stored in a suitable container for total organic carbon analysis.

The kinetic data were evaluated by pseudo-first and pseudo-second order models using the linear regression technique using the graphical method in an electronic spreadsheet.

Equations 1 and 2 present, respectively, the pseudo-first-order and pseudo-second-order models, where k is the pseudo-first-order adsorption rate constant (min^{-1}) or pseudo-second order (g.mg^{-1}.min^{-1}), qe is equilibrium adsorption capacity (mass of adsorbate per mass of adsorbent, mg. g^{-1}) and q(t) is the adsorption capacity in one time: t (mg. g^{-1}).

$$\frac{dq(t)}{dt} = k\,(q_e - q(t)) \qquad \text{Equation (1)}$$

$$\frac{dq(t)}{dt} = k(q_e - q(t)^2) \qquad \text{Equation (2)}$$

Such models were chosen to test whether the adsorption kinetics is primarily controlled by external diffusion, and is independent of the concentration of the adsorbate (pseudo-first order model), or whether it is dependent on the amount of chemical species adsorbed on the surface of the adsorbent and the amount adsorbed in the equilibrium state (pseudo-second order model).

RESULTS PRESENTATION

The results presented are related to tests carried out on a bench scale with commercial pulverized activated carbon produced from babassu coconut endocarp (CAP Babassu). The discussion (or analysis) of the results is carried out in the subsequent item.

The data obtained from the thermogravimetric analysis are presented in Figure 1, while Figure 2 presents the results of the pH$_{PCZ}$.
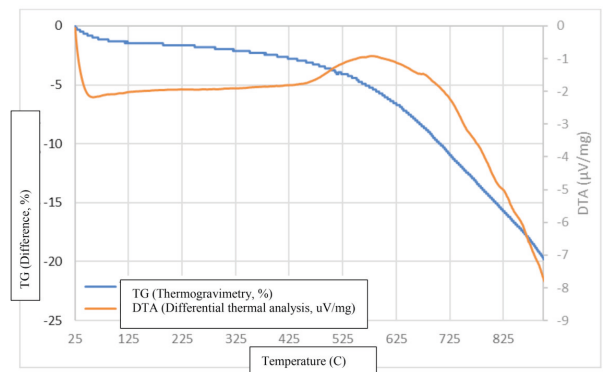

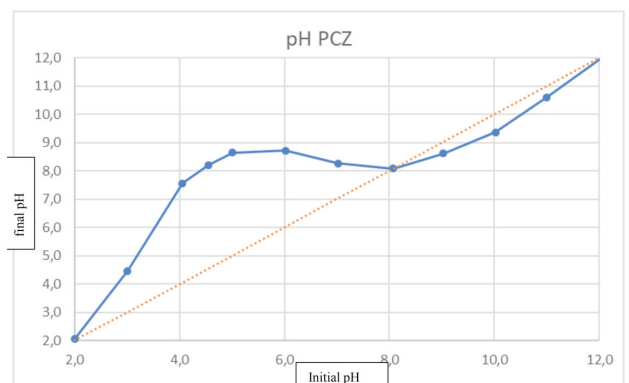Figure 1: Thermogravimetric analysis of CAP Babassu.

Figure 2: pH$_{PCZ}$ do CAP Babassu.

The CAP Babassu kinetics study generated four graphs that are presented in Figures 3 to 6. Figure 3 shows the behavior of the

concentration of residual PFOA (adsorbate) over the time of contact with CAP Babassu (adsorbent).
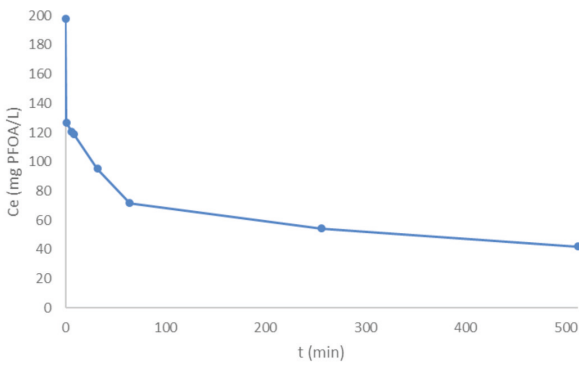

Figure 3: Residual concentration of PFOA throughout the adsorption kinetics test - CAP Babassu.

Figure 4 shows the fit of the data to the pseudo-first order kinetic model, where the Lagergren equation is used in its linearized form [$ln (q_e - q(t)) = ln (q_e) kt$] (Plazinski *et al.*, 2009). It was plotted $ln (q_e - q(t))$ depending on time *(t)* and using linear regression, a line graph was produced where the slope é k and $ln(q_e)$ the intercept. Figure 5 shows the adjustment of the data to the pseudo-second order kinetic model, which presents the following equation in its linearized form [$\frac{t}{q(t)} = \frac{1}{q_e^2 k} + \frac{1}{q_e} t$]. P It was plotted $\frac{t}{q(t)}$ in relation to time t and using a linear regression, a line graph was produced where the slope é $\frac{1}{q_e}$ and the intercept $\frac{1}{q_e^2 k}$.
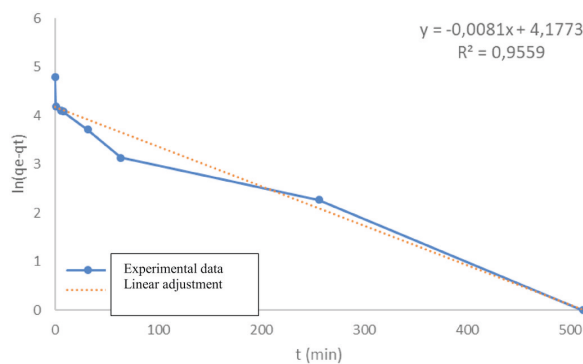

Figure 4: Adjustment to the pseudo-first order kinetic model [ln(qe-qt) as a function of time (t)] - CAP Babassu.
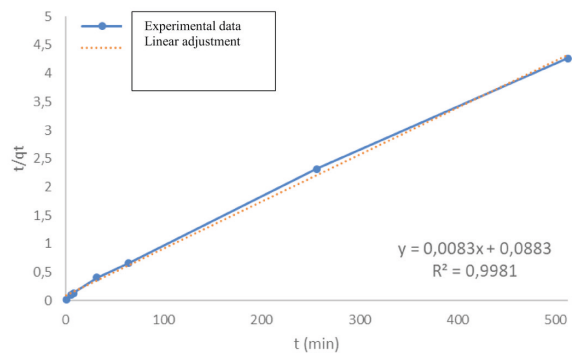

Figure 5: Adjustment to the pseudo-second order kinetic model [t/qt as a function of time (t)] - CAP Babassu.

Figure 6 presents the joint comparison of the equilibrium concentration data over time and the lines of each of the compared kinetic models.
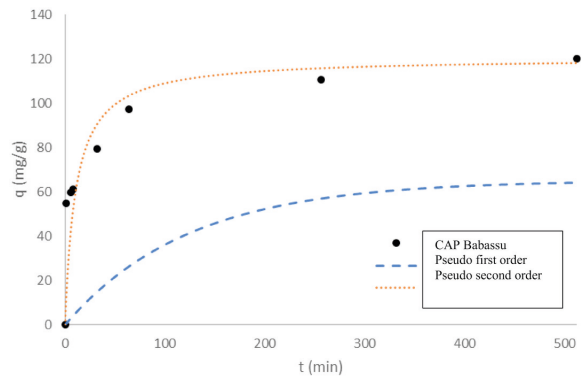

Figure 6: Comparison between equilibrium concentration data and the pseudo-first and pseudo-second order models obtained - CAP Babassu. Figure

Table 1 presents the parameters calculated for each model, as well as the coefficient of determination.

Pseudo-first order	k first order (min^{-1})	0,008100
	qe (mg. g^{-1})	65,19
	R^2	0,9559
Pseudo-second order	k second order (g.mg^{-1}.min^{-1})	0,000780
	qe (mg. g^{-1})	120,48
	R^2	0,9981

Table 1: Pseudo-first order and pseudo-second order kinetic parameters for PFOA adsorption.

DISCUSSION OF RESULTS

Data from thermogravimetric analysis (Figure 1) show some stability of the coal up to around 475ºC (probable synthesis temperature of the material), with the loss of mass from this temperature being accentuated by thermal degradation of the material's carbonaceous compounds.

Activated carbon presented a point of zero charge close to pH 8.0, and solutions with pH values below the PCZ cause the carbon to present a positive charge on its surface and thus favor the adsorption of negatively charged compounds through interactions physical and electrostatic. Solutions with pH values above the PCZ occur the opposite, favoring the adsorption of positively charged compounds.

Since the pKa of PFOA is approximately 2.5 (US Environmental Protection Agency, 2014), in solutions with higher pH values, PFOA appears in the ionized form with a negative charge, thus, in the pH range of na which the experiment was conducted, pH~ 6.5, in principle, physical and electrostatic interactions are favored.

Figure 3 shows a reduction in PFOA concentration of 126 mg. L-1 after 1 hour of contact time and 156 mg.L-1 at the end of 8.5h. Based on the data presented in Figure 3, adherence to the pseudo-first order and pseudo-second order models were tested (Figures 4 and 5).

The comparison of the coefficients of determination relative to the adjustments of experimental data to the models (0.9559 versus 0.9981 – Table 1) indicated that the pseudo-second order model proved to be adequate to represent the adsorption of PFOA on the activated carbon studied (CAP Babassu). Furthermore, the values calculated by the model were those closest to the actual test values (Figure 6), confirming the effective fit of the data to the model. This excellent fit to the pseudo-second-order model is also consistent with literature data for PFOA adsorption on other activated carbons (Inyang and Dickenson, 2017; Rattanaoudom et al., 2012).

CONCLUSIONS

Activated carbon from babassu coconut endocarp proved to be a potential adsorbent for use in the removal of PFOA (qe = 120 mg PFOA/g CAP babassu), following a pseudo-second order kinetic model, suggesting the predominance of chemical adsorption and coexisting with physical adsorption.

It is recommended that the same methodology be applied to other commercial charcoals produced in Brazil, aiming to compare and evaluate the influence of charcoal characteristics on PFOA adsorption.

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