Evaluation of adsorbend prepared from eucalyptus pruning wood fro quinoline removal in aqueous media via adsorptive processes

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Abstract

During the processing of petroleum, liquid toxic effluents are generated, such as quinoline. In view of the above, this work aims to evaluate the kinetic evolution and equilibrium adsorption of quinoline, in an aqueous medium, using activated carbon from eucalyptus pruning wood as an adsorbent. The adsorption kinetic evolution was rapid, reaching equilibrium in the first minutes. Both the pseudo-first order and pseudo-second order models well represented the experimental data, indicating that adsorption depends on both the available sites and the concentration of the adsorbate in solution. The Sips model presented the best fit to the experimental data, indicating adsorption in mono and multilayers, in addition to a heterogeneous surface and with a maximum adsorption capacity of 123 mg·g^{-1}. The values of R^2, S_{r^2} and n suggests that adsorption is favorable, and the active sites have different energy levels. In this way, the adsorbent prepared from biomass residue proved to be effective in removing quinoline.

Keywords: Adsorption; Agro-industrial waste; Biomass.

1. Introduction

Oil refineries play an important role in the production of goods for use, thus contributing to the structuring of Society. Oil goes through several processing stages (atmospheric distillation and vacuum distillation) and conversion (catalytic cracking and catalytic reforming). It is in these stages where a significant number of liquid effluents are generated, generally containing hydrocarbons, phenols, sulfur compounds, nitrogen compounds, oxygen compounds, as well as heavy metals [1, 2].

Among the nitrogenous aromatic compounds, quinoline stands out for being commonly found in fossil fuels. The removal of quinoline from effluents is crucial to avoid harm to fauna, flora and humans if it is discarded in receiving bodies without proper treatment [3].

Conventional effluent treatment methods (physical, chemical and biological) are inefficient for removing quinoline from aqueous media. Therefore, it is necessary to apply a process such as adsorption. This process stands out for its operational simplicity, as it does not require qualified labor, and for the possibility of using waste to produce the adsorbent, in addition to allowing the recovery of the quinoline after desorption [4, 5].

In view of the above, this work aimed to evaluate the kinetic evolution and equilibrium adsorption for the removal of quinoline in an aqueous medium using activated carbon prepared from eucalyptus pruning wood as an adsorbent.

2. Methodology

2.1 Preparation and quantification of the working solution

Quinoline stock solutions (NEON, 96%) were prepared at a concentration of 1000 mg·L^{-1}. Working solutions were obtained by diluting the stock solution. All reagents used to adjust pH and carry out the tests were of analytical grade. The quinoline contents were quantified before and after conducting the adsorption experiments using the ultraviolet-visible (UV-Vis) molecular absorption spectrophotometry technique (TermoScientific, Genesys 10S UV-Vis).

A spectral scan was performed in the range of 200-800 nm to identify the quinoline characteristic wavelength (λ). Based on it, na analytical curve was

built and the limits of detection and quantification were calculated, as well as the methods precision.

Blank assays were conducted for each experiment. The calculation fo the absorbed amount per mass of adsorbent (adsorptive capacity, q) was carried out using Equation (1).

$$q = \frac{(C_0 - C_f) \times V}{m} \qquad (1)$$

In which: C_0 and C_f are the initial and final concentrations of the adsorbate (mg·L^{-1}); V the volume of the solution (L) and m the adsorbent mass in gram (g).

2.2 Adsorbent preparation

Eucalyptus pruning wood charcoal was provided by Elephant LTDa company. Those were carbonized in a metal oven with an internal heating source for 4 h at 500°C. The chemical activation was carried out using phosphoric acid (H$_3$PO$_4$ 85%, Vetec brand), in a 5:3 (M/V) ratio, in a refractory container, and homogenized using a glass rod. Then, the mixture was placed in a muffle furnace (Quimis brand) with a hating ramp (10°C·min^{-1} at 100°C/30 min, 200°C/1 h and 350°C/1h).

After cooling, the activated carbon was washed by immersion in a 1% NaHCO$_3$ solution (FMaia) to remove residual acid until the pH of the solution reached between 6 and 7. It was then washed with distilled water and dried in an oven at 105ºC for 24 hours. The prepared adsorbent was called eucalyptus activated carbon (EAC) and classified using a series of Tyler sieves.

2.3 Kinetic Evolution of the adsorptive process

Based on the parameters established in previous studies (pH of the solution equal to 5, granulometry less than 0.09 mm, stirring speed of 200 rpm and mass ratio of the adsorbent and volume of the solution equal to 1 g·L^{-1}), studies were carried out to evaluate the kinetic evolution of adsorption.

The tests consisted of placing the adsorbent in contact with solutions containing quinoline at 30 mg·L^{-1} at time intervals ranging from 0 to 360 minutes. Pseudo-first order (Equation 2) and pseudo-second order (Equation 3) kinetic models were fitted to experimental data [5].

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (2)$$

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (3)$$

In which: k_1 the pseudo-first order adsorption rate constant (min^{-1}); q_e and q_t the adsorptive capacities at equilibrium and at time t; k_2 the pseudo-second order adsorption rate constant (g·mg^{-1}·min^{-1}).

The model adjustments to experimental data were performed using Origin 8.5 software using nonlinear adjustment methods. The quality of model adjustments was assessed by calculating the residual values left by the models (Sr^2) and the linear regression coefficients (R^2).

2.4 Adsorptive equilibrium

The adsorption equilibrium tests were conducted within the equilibrium time established in the previous study and under the operating conditions previously defined and used in the study of the kinetic evolution.

Quinoline solutions with concentrations ranging from 1 to 250 mg·L^{-1} were added to the EAC adsorbent, maintaining the temperature at 30 ± 2°C. To evaluate the adsorption process, the Langmuir (Equation 4), Freundlich (Equation 5) and Sips (Equation 6) models were applied.

$$q = \frac{q_{máx} K_L C_e}{1 + K_L C_e} \qquad (4)$$

$$q_e = K_F C_e^{\frac{1}{n}} \qquad (5)$$

$$\frac{q_e}{q_{máx}} = \frac{(K_s C_e)^n}{1 + (K_s C_e)^n} \qquad (6)$$

In which: q is the adsorption capacity of the material (mg·g^{-1}); K_L is the Langmuir model equilibrium adsorption constant (adsorbate/adsorbent interaction constant in L·mg^{-1}); $q_{máx}$ is the maximum adsorptive capacity; K_F is the adsorption constant of the Freundlich model [mg·g^{-1}(L·mg^{-1}) n^{-1}]; q_e is the adsorption capacity at equilibrium (mg·g^{-1}) and n is the constant related to the heterogeneity of the material surface; K_s is the adsorption constant of the Sips model (mg·g^{-1}). The evaluation of the models followed a similar procedure to that of the kinetic models described previously.

3. Results and discussion

3.1 Assessment of kinetic evolution

In order to evaluate the kinetic evolution in the adsorptive process, the curve with the experimental data and the adjustments of the pseudo-first order (PFO) and pseudo-second order (PSO) models are presented in Figure 1.
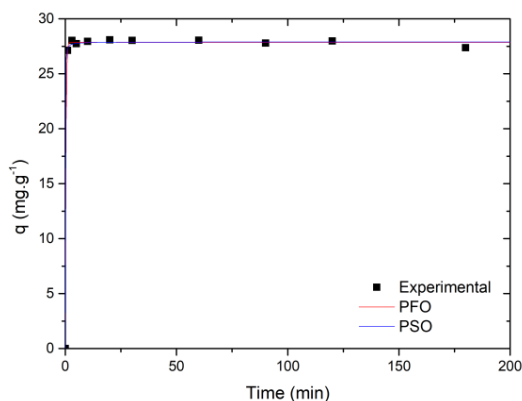

Fig.1. Kinetic evolution of quinoline fitted to model. Conditions: $C_0 = 30$ mg$\cdot$L^{-1}; pH = 5; 360 min; 30 ± 2 °C.

Based on Figure 1, it can be inferred that the kinetic evolution was rapid, reaching equilibrium in the first minutes. In order to ensure that the system is in balance, the adsorption equilibrium study was carried out for 60 min.

It is observed that the kinetic models obtained a good fit to the experimental data. Table 1 shows the parameters calculated from the non-linear regression of the PFO and PSO kinetic models.

Table 1. Parameters of the PFO and PSO models for quinoline adsorption by EAC.

Models	Parameters	Results
PFO	q_e (mg$\cdot$g^{-1})	27.86 ± 0.06
	k_1 (min^{-1})	3.63 ± 0.34
	Sr^2	0.998
	R^2	0.999
PSO	q_e (mg$\cdot$g^{-1})	27.89 ± 0.08
	k_2 (min^{-1})	1.56 ± 0.71
	Sr^2	0.998
	R^2	0.998

Analyzing the data in Table 1, it can be seen that the PFO and PSO models presented an $R^2 > 0.99$ and equal Sr^2 values, indicating that the quinoline adsorption process follows a behavior with non-linear driving forces. Furthermore, it is noted that the pseudo-second order model takes longer to reach equilibrium, as its kinetic constant is directly related to the mass transfer speed between the phases, while the pseudo-first order model constant indicates a faster balance.

3.2 Adsorptive equilibrium

The adsorption equilibrium evaluation makes it possible to calculate the maximum adsorption capacity for the adsorbent. Figure 2 presents the adsorption equilibrium isotherms for quinoline, together with the adjustments of the evaluated models.
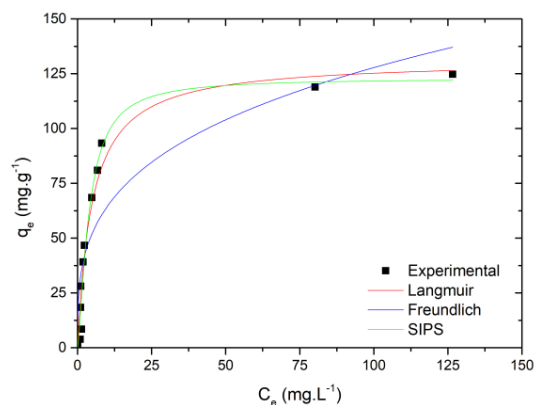

Fig.2. Quinoline adsorption equilibrium by EAC, with the adjustment curves of the adsorptive models. Conditions: pH=5; 60 min; 200 rpm, 1 g$\cdot$L^{-1} e 30 ± 2°C

As shown in Figure 2, the shape of the curve corroborates the result of the kinetic study with a type of isotherm described by a behavior of rapid initial increase followed by a slow stage until reaching stability.

The parameters of the evaluated models are presented in Table 2.

Table 2. Parameters of the Langmuir, Freundlich and Sips models for quinoline adsorption by EAC.

Modelos	Parâmetros	Resultados
Langmuir	q_e (mg·g^{-1})	131 ± 8
	$K_L (L·mg^{-1})$	0.20 ± 0.03
	Sr^2	0.926
	R^2	0.952
Freundlich	n	3.4 ± 0.6
	K_F (mg·g^{-1})·(g·L^{-1})$^{-1/nf}$	32 ± 6
	Sr^2	-
	R^2	0.795
Sips	$q_{máx}$ (mg·g^{-1})	123 ± 6
	n	1.3 ± 0.1
	$K_S (L·g^{-1})$	0.15 ± 0.03
	Sr^2	0.612
	R^2	0.968

Based on the data in Table 2, it is observed that the Sips model was the one that best represented the experimental data with the highest R^2 value and lowest Sr^2. This suggests that the adsorption process occurs in both mono and multilayers and that the surface of the material is heterogeneous, with active sites of different energy levels. Furthermore, the values of n suggest that adsorption is favorable.

4. Conclusion

From the results obtained, it can be concluded that the adsorbent prepared from eucalyptus pruned wood demonstrated a high efficiency in removing quinoline from aqueous media. The kinetic evolution indicated that the adsorption process follows a complex behavior with nonlinear driving forces. Furthermore, multilayer adsorption can occur, with the surface of the adsorbent being heterogeneous. The favorable adsorption behavior, indicated by the n values, reinforces the potential of the eucalyptus pruned wood adsorbent as an effective and sustainable alternative for treatment aimed at removing quinoline.

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