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Biosorption of Chlorothalonil on Fique's Bagasse *(Furcraea sp.)*: Equilibrium and Kinetic Studies

Adriana María Quinchía-Figueroa[1], Margarita Enid Ramírez-Carmona[2] and Geovanna Tafurt-García[2]

1. Ingeniería Ambiental, Escuela de Ingeniería de Antioquia, Medellín 7516, Colombia

2. Centro de Estudio y de Investigación en Biotecnología, Universidad Pontificia Bolivariana, Medellín 56006, Colombia

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Abstract: The bagasse generated as residue during the process of fiber extraction of the fique or sisal (*Furcraea sp.*) has been evaluated in raw state, washed and thermally activated for the adsorption of chlorothalonil (CLT). The study was developed at 25 ℃ the effects of contact times, biomass dose and pH were investigated. The bagasse was characterized using Scanning Electronic Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). A significant change in the signal spectroscopics was found in the thermally activated material. The experimental data obtained in this study shows that the fique's bagasse is a material with potential to be used in adsorption of pollutants. The maximum uptake was 57.143 mg/g for the thermally activated material. This outcome constitutes a good contribution in environmental and technical terms.

Key words: Chlorothalonil, biosorption, fique's bagasse, pesticides.

1. Introduction

The growth of the world population and the need to extend the food coverage has increased the production and application of insecticides in the last 50 years; due to this, environmental problems that have repercussions on the human health have been generated [1].

The pesticides can be classified in four groups according to the grade of toxicity, since depend on its structure can generate several adverse effects in living [2]. The groups I and II include highly poisonous substances that generate an immediate environmental damage, and in the groups III and IV are found substances with long term effect than act of irreversible form [3].

The chlorothalonil (2,4,5,6-tetrachloro-1,3-benceno dicarbonitrilo, CLT), known as Bravo or Daconil, is an aromatic polychlorinated pesticide of broad spectrum, non-systemic. In the USA., the CLT is the second fungicide most widely used for agricultural in crops such as tomato, cotton, potatoes, beans, household level, and even golf camps [4, 5]. It is classified by the U.S. Environmental Protection Agency (U.S. EPA) as a "probable human carcinogen" [3]; its chemical structure makes it hardly degradable and recalcitrant. CLT can affect the physiology of soil microorganisms causing significant consequences on ecosystems, such as nitrogen dynamics and cycle of nutrients [6, 7]. One important aspect is that the 4-hydroxy-2,5,6-tricloroisoftalonitrilo, metabolite obtained from CLT, is more dangerous, mobile and toxic than its parental compound. So, techniques as adsorption, immobilization or degradation (chemical or biological) might be important for diminishing the impact environmental and to reach the health of ecosystems exposed to CLT and its metabolites [6, 8].

Adsorption has been used as a technique for removing pollutants. Among, the adsorbent materials more used in aqueous systems and industrial effluents are activated carbon, anthracite and zeolite. However,

Corresponding author: Adriana María Quinchía-Figueroa (1967-), female, agricultural engineer and environmental engineer MSC, research fields: environmental engengieering and soil pollution biodegradation. E-mail: a.quinchia@yahoo.com.

since the removal of pollutants in agricultural areas must be cheap and compatible with ecosystems, the option of lignocellulosic materials due to their physical and chemical characteristics has become an alternative with good results for adsorption of dyes, heavy metals, hydrocarbons and pesticides [9]. Among lignocellulosic materials studied are the sugar cane fiber, pine bark, water buchon (*Eichornias crassipes*), scrape grape, fruit peels and coffee grounds [9-16]. Nevertheless, bagasse produced in the extraction of fique's fiber (*Furcraea sp.*), which accounts for 17% of the leaf have not been studied yet in adsorption of pollutants [17].

The aim of the present work was to investigate the equilibrium and kinetic of the fique's bagasse as adsorbing material in raw state, washed and thermally activated (RFB, WFB, ACFB). The effects of superficial modifications were analyzed by Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electronic Microscopy (SEM). While Gas Chromatography coupled to micro-Electron Capture Detector (GC-μECD) was used for analyzing the effects of contact times, biomass dose and pH. Langmuir and Freundlinch models were tested to interpret the adsorption isotherms.

2. Materials and Methods

2.1 Materials

The fique's bagasse (*Furcraea sp.*) was supplied by the Compañía Nacional de Empaques, from "El Pantanillo" village of Barbosa's town (Antioquia, Colombia). The tetrachloroisoftalonitrilo (99%, Chem. Service, West Chester) was used for quantification by GC-μECD. The stock solution of CLT for adsorption tests was prepared in distilled water with Daconil 720 SC (Syngenta, Colombia). The solvents used were analytical grade (Panreac).

2.2 Preparation and Characterization of the Adsorbent

The fique's bagasse (FB) was dried in air with turns each 12 hours, homogenized in size in a blender and sieving through mesh # 30 (1.86 mm). The FB was used raw (RFB, without treatment or modification), washed (WFB) and as activated carbon (ACFB). The WFB was got from FB by washing with distilled water and agitation to 350 rpm for 48 h. The solid residue was dried in oven at 60 ℃ for 6 h (TAPI standard 204) [18]. The batch experiments for adsorption were performed in 50 mL beakers. The sampling was conducted during predetermined time intervals. The adsorbent material was mixed with CLT solutions (20 mL) and agitated at 350 rpm. The tests were conducted with the following parameters: initial CLT concentration of 40 mg/L, pH between 2 and 10, adsorbent doses between 3 and 8 g/L and time periods ranging from 5 mins to 2 h. Predetermined ranges of the parameters evaluated (initial CLT concentration, adsorbent doses and pH) were defined based on preliminary adsorption tests. All tests were performance in three replicates. The isotherms of adsorption were assessed for CLT concentrations varied between 1 and 460 mg/L.

2.3 Analysis of Chlorothalonil

An aliquot (1 mL) was taken from beaker after contact time with the bioadsorbent for analyzing CLT concentration. A mix of hexane: acetone (1:1, v:v; 1 mL) was used as extraction solvent. 1 μL of organic phase was taken for quantification by GC-μECD.

The CLT analysis and detection was assessed in a gas chromatograph Agilent 6890N (Agilent Technologies, Palo Alto, California, USA) coupled to a μ-ECD, equipped with two injection ports split/splitless (split 5:1), manual injection system and a computerized data system GC ChemStation Rev. A.09.03 [14, 17] (Agilent Technologies, Palo Alto, California, USA).

It used an HP-5 column (Hewlett-Packard, Palo Alto, California, USA), stationary phase 5% phenylpolimethylsiloxane (30 m × 0.32 mm (id) × 0.25 μm (d_f)) and Helium (99.995%, Aga Fano SA, Medellín, Colombia) as carrier gas (1.3 mL/min, 50 ℃) with an inlet pressure in the column head of 9.53 psi. The oven temperature was programmed from 150 ℃ (1 min), then 20 ℃/min to 300 ℃ (2 mins). The injector was programmed to 270 ℃ with a helium mass flow of 67.6 mL/min. The detector temperature was 280 ℃ and nitrogen flow of 37 mL·min^{-1}.

2.4 Adsorption Isotherms

The adsorption isotherms were carried out for biomass concentrations of 6 g/L, contact time of 120 mins for RFB and WFB, and 30 mins for ACFB, without change of pH. Eq. (1) was used to evaluate the efficiency of adsorption [21].

$$q = [V(C_i - C_F)]M^{-1} \quad (1)$$

Where; q: Uptake of pollutant (mg) per gram of bioadsorbent (g), (mg/g); C_i: Initial pollutant concentration, (mg/L); C_F: Final or equilibrium pollutant concentration, (mg/L); V: Volume of the contaminant solution, (L); M: Bioadsorbent mass (g).

The Langmuir and Freundlich models were tested for equilibrium description. Eq. (2) is used to describe the Langmuir model [22]:

$$q_e = [q_{\max} K_L C_e][1 + (K_L C_e)]^{-1} \quad (2)$$

Where q_e (mg/g) expresses adsorbed CLT (mg) per gram adsorbent material at equilibrium; C_e (mg/L) is the CLT concentration in solution at equilibrium; q_{max} (mg/g) and K_L (L/mg) are constants related to the capacity and energy of adsorption, respectively.

The Freundlich model can be described by Eq. (3) [22]:

$$q_e = K_F C_e^{1/n} \quad (3)$$

Where, K_F and n are constants that indicate the capacity and relative adsorption intensity, respectively.

3. Results and Discussion

3.1 Adsorbent Characterization

The images of raw fique's bagasse, washed and thermal activated (RFB, WFB, ACFB, respectively) are shown in Fig. 1, it appears that both treatments (washing and thermal) modify the superficial morphology of the bagasse. Since FB is a residue from the extraction of fiber from the leaf of the fique's plant (*Furcraea sp*.), there are mix of short fibers and parenchyma (Fig. 1, 1a-1c). The RFB is characterized by a smooth and less porous surface with some holes own the bagasse, showing amorphous zones and some superficial spiral cellulose structures (Fig. 1, 1a-1c). In WFB, the surface roughness increases relative to RFB due to the removal of substances such as gums, sugars and dyes by washing (Fig. 1, 2a-2c). The ACFB SEM photographs is revealed an effective and severe modification of the surface of the FB with a more porous structure due to the thermal treatment which is related to a substantial increase in the superficial area (Fig. 1, 3a-3c) [18-20].

The infrared spectroscopy (FTIR) was employed to obtain information on chemical structure and functional groups present in the surface of RFB, WFB and ACFB. In this case, the signals of FTIR spectra are similar to those reported in the literature for materials such as coffee beans, palm tree leaves and olive waste cakes [19, 20, 22]. The signals were located in the following ranges of frequencies: 1000-1029 cm^{-1}, for the elongation of the C-O group; 1400-1600 cm^{-1}, for the stretching of C=C bond; 1726 cm^{-1}, due to tensions of C=O group; 2850-2915 cm^{-1}, corresponding to stretching of aliphatic C-H bond of RFB and WFB materials, and between 3000-3500 cm^{-1}, associated with the elongation of O-H bond [23, 24]. In ACFB, due to thermal activation is note the decrease in -OH groups, the disappearance of C=O, $-CH_2$, and $-CH_3$ groups, and the increasing in C=C functional groups which are characteristic of aromatic structures [23, 24].

3.2 Effect of Solution pH

The adsorption processes and in particular those of biosorption are generally strongly dependent on pH. The effect of pH variations between 2 and 10 was observed for RFB and WFB, with a biomass dose of 6 g/L and CLT concentration of 40 mg/L. The highest CLT adsorptions were 31.85% for the RFB at pH of 3, and 30.1% for the WFB at pH 2. In blank tests (*i.e.*

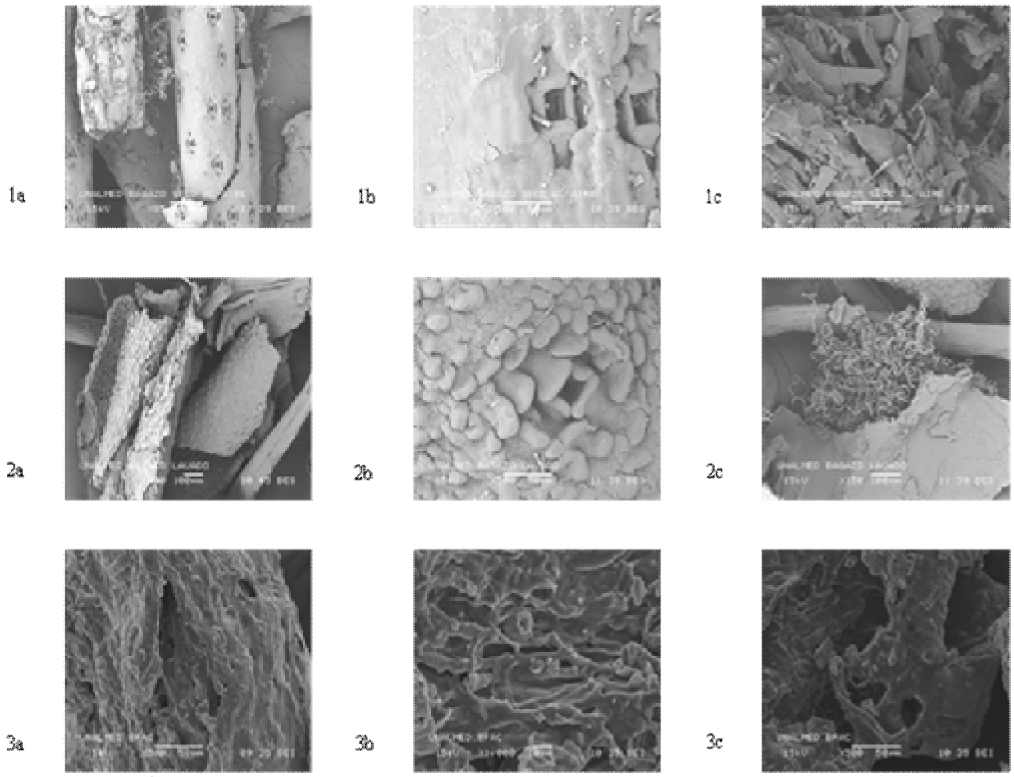

Fig. 1 SEM photographs of Raw Fique's Bagasse, RFB (1a-1c); Washed Fique's Bagasse, WFB (2a-2c); and Activated Fique's Bagasse, ACFB (3a-3c).

without changes in pH), adsorption values were relatively high (RFB: 29.5% and WFB: 18.8%) compared with another pH test; because of this, the adsorption tests were performed without modification of pH.

3.3 Influence of Contact Time on Chlorothalonil Adsorption

The effect of contact time was studied between 5 and 240 mins, an initial CLT concentration of 40 mg/L and a biomass dose of 6 g/L, without changing pH. The equilibrium times were achieved at 120 min for RFB and WFB, and 30 mins for ACFB (Fig. 2). This behavior can be explained by the change in superficial structure as could be seen in the images of SEM and FTIR spectra.

Fig. 2 shows that the kinetics is characterized by two Phases. Firstly, there is a rapid adsorption which is described by a physical mechanism of superficial retention. For RFB and WFB, this stage is between 0 and 60 mins, with a CLT adsorption of 31 ± 1.7 and 48 ± 1.8%, respectively. For ACFB, this phase occurs between 0 and 30 mins, reaching a maximum adsorption of 99.7 ± 0.14%. The second phase is characterized by slow kinetics with a slight increase in the percentage of adsorption, due to the saturation of the superficial active sites. The adsorption that occurs at this stage can be explained by mechanisms such as intra-particle diffusion [20].

3.4 Influence of Adsorbent Dosage

The effect of biomass dose between 3 and 8 g/L, for an initial CLT concentration of 40 mg/L, contact time of 120 mins for RFB and WFB and 30 mins for the ACFB was studied. The percentage of adsorbed CLT showed a proportional increase in relation to the biomass content, a fact that may be attributable to the increase of contact area and active sites. The maximum adsorption of CLT were 33.8 ± 0.6, 42 ± 4 and 99.1 ± 0.1% for RFB, WFB and ACFB, for biomass dose of 6, 7 and 6 g/L, respectively (Fig. 3). The CLT uptake capacity per gram of biomass (mg/g) decreases, due to decrease of effective superficial area (ratio adsorbate / adsorbent), as it is shown in Fig. 4. Similar behavior was reported in the literature for adsorbents such as coffee beans [19], palm leaves [20] and residual olive cake [22]. The ACFB presented CLT uptake values ranging from 8.6 ± 0.3 to 3.3 ± 0.2 mg/g.

3.5 Adsorption Kinetics

The adsorption isotherms performed at 25 °C are shown in Fig. 5. The uptake capacity of CLT from aqueous solutions by RFB and WFB was lower compared with other similar residues such as shown in Table 1. However, the shapes of the curves indicate a favorable adsorption with an increase in uptake capacity. In the thermally activated material, uptake is noticeable, which it potentiates for these processes.

The Langmuir and Freundlich models were used to describe the adsorption of CLT in RFB, WFB and ACFB. The coefficients and the maximum uptake capacity of CLT (q_{max}) are shown in Table 2.

Base on the values of R^2 (linearity of model) and E (error of fit, which represents the deviation between experimental and estimate data), RFB was better described by the Freundlich model, while WFB and ACFB were by the Langmuir model. The Freundlich model is empirical and is based on the assumption that adsorption occurs on heterogeneous surfaces. The parameters K and n obtained from the linearization of this model (Eq. (3)), indicate the capacity and intensity of adsorption, respectively. So, when the value of n is greater than one, often display a favorable adsorption and the heterogeneous nature of the adsorbent surface, as in the case of RFB (Fig. 6). Using the The Langmuir model (Eq. 2), it is considered that the adsorption on the surface occurs in monolayers, with a finite number of identical sites and uniform adsorption energy, which agrees with the superficial characteristics of WFB and ACFB regarding RFB and consequently, the q_{max} is higher for the first two, due to surface modifications [19, 20].

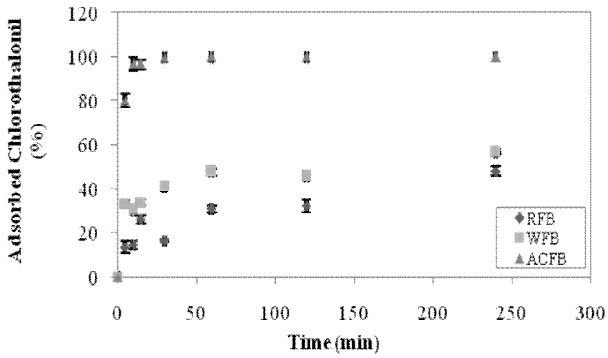

Fig. 2 Influence of contact time on CLT adsorption (biomass concentration of 6 g/L, CLT concentration of 40 mg/L, and percentage of adsorbed CLT mg/g).

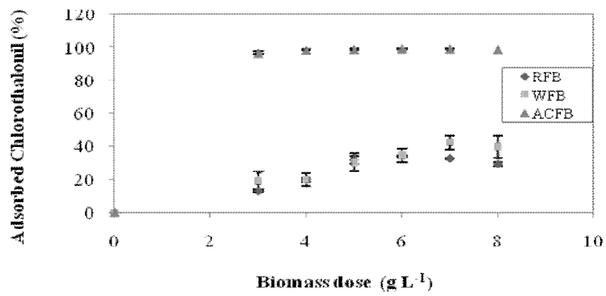

Fig. 3 Effect of biomass dose for RFB, WFB and ACFB (contact time 120, 120 and 30 mins for RFB, WFB and ACFB, respectively; initial CLT concentration of 40 mg/L).

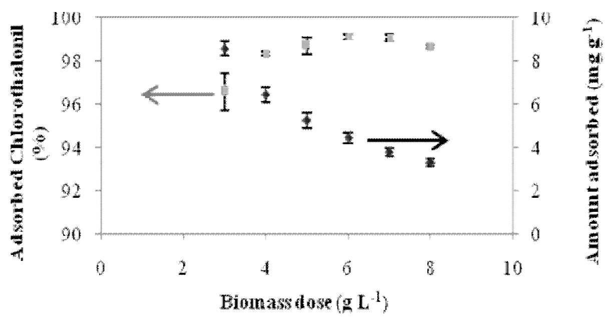

Fig. 4 Effect of biosorbent dose for ACFB (contact time 30 mins, initial CLT concentration of 40 mg/L).

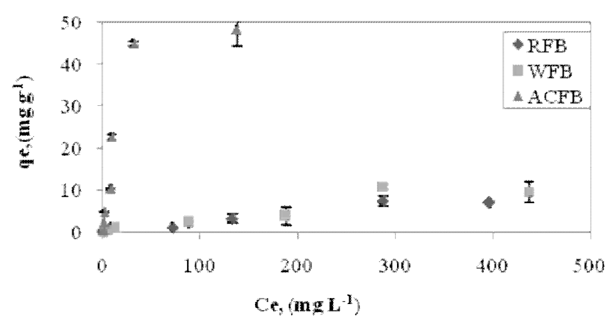

Fig. 5 Adsorption isotherm of CLT by RFB, WFB and ACFB (contact time 120, 120 and 30 mins for RFB, WFB and ACFB, respectively, initial CLT concentration of 1-460 mg /L, adsorbent dose of 6 g/L).

Table 1 Comparison of different levels of adsorption for residual materials.

Material	Adsorbate	Uptake (mg/g)	Reference
RFB	CLT	7 ± 1	This study
WFB	CLT	10.9 ± 0.6	This study
ACFB	CLT	48 ± 4	This study
Coffee cakes activated	Methylene blue	14.9	[19]
Cellulose of orange peel	Cu^{2+}	1.22 (mol/kg)	[25]
Palm leaves	Zn^{2+}	14.6	[20]
Olive cake (unmodified activated carbon)	Cu^{2+}	12.0	[22]
Olive cake (modified activated carbon)	Cu^{2+}	35.3	[22]

Table 2 Kinetic parameters for CLT adsorption by RFB, WFB and ACFB.

Model	Parameter	Material		
		RFB	WFB	ACFB
Langmuir	q_{max} (mg/g)	6.042	12.136	57.143
	K_L (L/mg)	0.767	0.008	0.073
	R^2	0.886	0.895	0.957
	E (%) *	45.410	2.131	3.025
Freundlich	K $(L/mg)^{1/n}$(mg/g)	0.293	0.020	25.246
	n	2.541	1.488	1.658
	R^2	0.973	0.995	0.963
	E (%)	33.189	79.171	409.6726

*E= Error of fit (%) = $[\sum(C_e \text{ experimental} - C_e \text{ estimade})^2/\sum(C_e \text{ experimental})^2]\times 100$

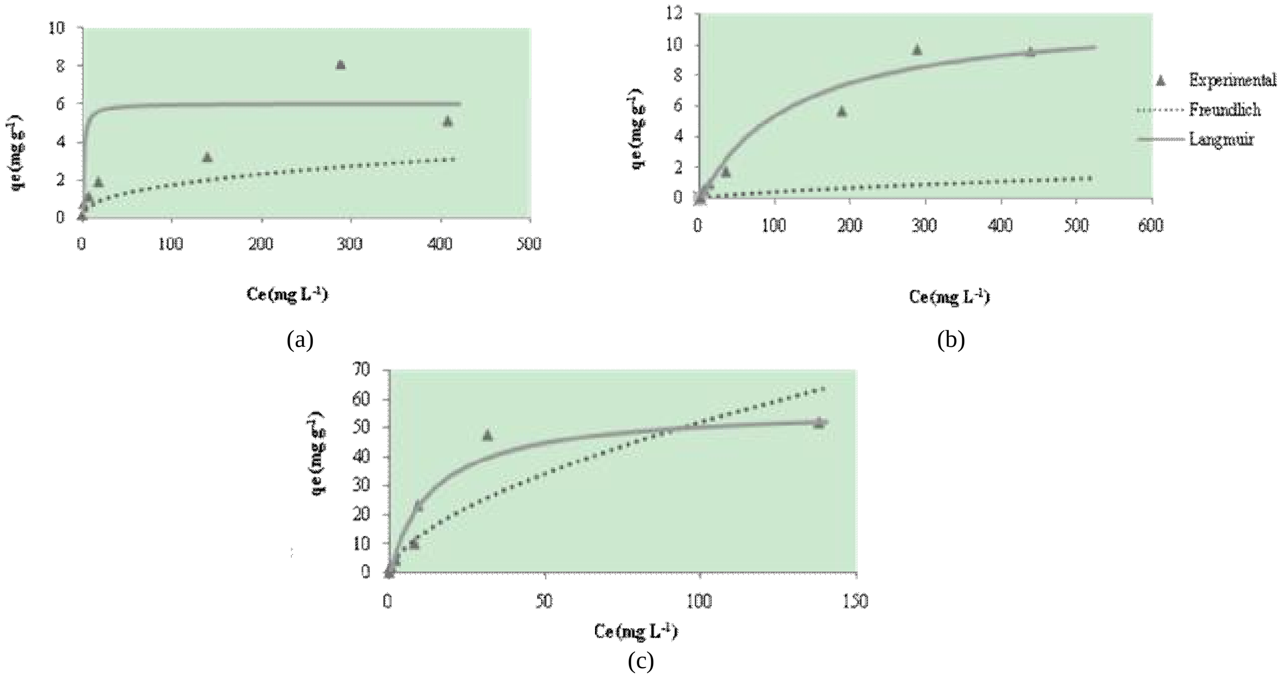

Fig. 6 Experimental adsorption isotherms of CLT by RFB (a), WFB (b) and ACFB (c) and estimated by the Langmuir and Freundlich models (contact time 120, 120 and 30 mins for RFB, WFB and ACFB, respectively; initial CLT concentration of 1-460 mg/L, adsorbent dose of 6 g/L and temperature of 25 ℃).

4. Conclusions

The experimental data obtained in this study show that raw fique's bagasse, washed and thermally activated (RFB, WFB and ACFB), have the potential to be used in the adsorption of polychlorinated pesticides such as chlorothalonil, which is a relevant contribution in environmental and technical terms. The surface modification due to the processes of washing and thermal activation causes an increase in the adsorption capacity ranging from 6.042 to 57.143 mg/g, which is comparable with other modification processes reported in the literature for similar waste materials. Data from the equilibrium indicate that the RFB shows a favorable adsorption than can be described by the Freundlich model, while RFB and WFB were best fit to Langmuir model, given the superficial characteristics.

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