

Adsorption of 5.5'-Disulfonicindigotin (5.5'-DI) onto Green Coconut Fiber (*Cocos nucifera* L.): Kinetic and Isotherms

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Abstract

Green coconut fiber (*Cocos nucifera* L.) has been largely used in solid-phase extraction. The effect of the initial dye concentration (1.91, 3.02 and 4.02) × 10⁻⁵ mol·L⁻¹ and solid phase contact (SPE) time were evaluated at different temperatures (283, 298 and 313) K at pH 2. Kinetic experimental data were applied to three simplified kinetic models: pseudo-first order, pseudo-second order, and intraparticle diffusion. The adsorption of 5.5'-DI onto the solid phase showed excellent fit to the pseudo-second order model. At 283, 298 and 313 K the maximum sorption, $q_{max,exp}$, for the lowest initial concentration ($C_0 = 1.91 \times 10^{-5} \text{ mol·L}^{-1}$) of 5.5'-DI were (5.01, 5.24 and 6.14) × 10⁻⁴ g·g⁻¹; for $C_0 = 3.02 \times 10^{-5} \text{ mol·L}^{-1}$ (0.93, 1.01 and 1.03) × 10⁻³ g·g⁻¹ and for $C_0 = 4.02 \times 10^{-5} \text{ mol·L}^{-1}$ (1.32, 1.40 and 1.49) × 10⁻³ g·g⁻¹, respectively. The adsorption of 5.5'-disulfonicindigotin (5.5'-DI) onto green coconut fiber has been investigated and the experimental equilibrium data were fitted to the Langmuir, Freundlich and Dubinin-Radushkevich models at different temperatures (283, 298 and 313) K. The evaluation of the mean sorption energy characterized the adsorption as physical and the adsorbent surface energetically homogeneous (n < 1). Thermodynamic studies show adsorption process to be endothermic ΔH^0 (+11.6 kJ·mol⁻¹) and spontaneous ΔG^0 (-9.7 kJ·mol⁻¹ at 283 K, -10.8 kJ·mol⁻¹ at 298 K and -11.9 kJ·mol⁻¹ at 313 K).

Keywords

5.5'-Disulfonicindigotin, Green Coconut, Isotherm and Kinetic Modeling

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1. Introduction

Coconut palm is cultivated in more than 90 tropical countries and it represents an important source of income [1]. Approximately 60 million tons of coconut (*Cocos nucifera* L.) were produced worldwide in 2010: 85% in Asia, 8.5% in the Americas, 2.9% in Africa and 3.2% in Oceania [2] [3]. The whole coconut tree may be used, but the main products are obtained from the fruit such as copra and oil, coconut milk, lauric acid, fiber, flour and coconut water (from immature fruit). These main products have several applications, e.g. composites, soaps, beverages, animal feed, detergents and cosmetics [4].

Green coconut husk is an agricultural residue whose high potential for use has yet to be explored in Brazil [5]. This residue corresponds to about 85% of the fruit and has become a serious environmental problem due to its slow degradation [6] and large volume of waste generated and discarded into landfills in Brazil. The decomposition of coconut husks generates methane, which is one of the most responsible gases for global warming [7].

Coconut husk can be processed to the condition of fiber, which is composed of cellulose, hemicellulose, lignin, pectin and various minerals. This fiber can be used in the preparation of composites such as bioplastics, natural adsorbent and as a source of raw materials for several processes [8]. It represents an alternative low-cost (bio)adsorbent and may be used for the removal of pollutants (metal ions, dyes and other natural and inorganic substances) present in wastewater. The retention capacity of several metallic ions in aqueous solution has been previously reported using coconut fiber as the adsorbent [9].

The environment is highly impacted by a significant volume of wastewater (not always treated accordingly before discharge) produced by the textile industry [10]. Some dyes and organic compounds from effluents of textile industries contain a high level of toxicity, and their removal is hampered by the stability of the compounds; they do not break down in light or heat and most of them are not biodegradable, thus causing serious problems to the aquatic life in lakes, rivers and seas.

Therefore, appropriate procedures for the removal of colored dyes from wastewater must be obtained [11] [12]. Kyzas *et al.* reported a review about changes from past to the future for adsorbent materials in treatment of dyeing wastewaters [13].

This study aims to use coconut fiber as a (bio)adsorbent for retention of the organic compound 5.5'-disulfonicindigotin (5.5'-DI), sulphonated species of Indigo blue dye (Figure 1) at different temperatures (283, 298 and 313) K.

Four simplified kinetic models including pseudo-first-and -second-order [14]-[16] equations and the intraparticle diffusion [17] were used to describe the adsorption processes. Adsorption equilibrium was described by using three commonly applied mathematical expressions: Langmuir [18], Freundlich [19] and Dubinin-Radushkevich [20] isotherm models.

2. Materials and Methods

2.1. Reagents and Solutions

All reagents and solvents used were of analytical grade. Distilled deionized water (Milli-Q) was used to prepare solutions. Indigo blue dye ((3H-indole-3-one2-(1.3-dihydro-3-oxo-2H-indol-2ylidene)-1.2-dihydro) is known in literature as CI Vat Blue or D&C no.6 and is used to dye natural and synthetic fibers. It is a blue crystalline solid with the molecular formula $C_{16}H_{10}N_2O_2$ (262.27 g·mol⁻¹), CAS Number 482-89-3 and a melting point between 300°C and 303°C. To prepare 5.5'-disulfonic indigotin solution ($C_{16}H_8N_2O_8S_2$), 466.36 g·mol⁻¹, 1.05 g of the Indigo blue dye (Sigma Aldrich) was added to 35 mL of concentrated H₂SO₄ while stirring.

The sulphonated species is obtained according to the chemical reaction (Figure 2). The temperature was kept at 80°C. And after cooling, the solution was diluted to 1000 mL with deionized water [12].

2.2. Biosorbent Material Preparation

Green coconuts (*Cocos nucifera* L.) were grown in Brazil northern state of Paraiba and purchased at Ceasa (Supply Center of Santo Andre, Brazil) [1]. Physicochemical properties of the adsorbent are show in Table 1 [21] [22].

The fruits were washed and cut in two halves. To obtain the fibers, the coconuts used were initially drilled to remove the water and then cut to remove the pulp. The bark was first ground in a toothed rollers mill to remove water, and then shredded in a hammer mill and placed in an oven at 378 K for a period of approximately six



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Cellulose (%)	23 - 43
Hemicellulose (%)	3 - 12
Lignin (%)	35 - 45
Electrical conductivity	$1.8 \text{ dS} \cdot \text{m}^{-1}$
Average diameter (µm)	157
Relationship (C/N)	132
Specific area $(m^2 \cdot g^{-1})$	362
Dry/Wet density (g·cm ⁻³)	1.15 - 1.45

hours. The fiber was then fractionated and stored in a suitable container. No chemical or physical treatments were performed prior to adsorption experiments.

2.3. Apparatus

The UV-Vis spectra were measured on a Shimadzu Model UV-2600 spectrophotometer using 1.00-cm quartz cells. All cuvettes, glass and plastic vessels were washed with a 10% (v/v) HNO₃ aqueous solution followed by distilled and deionized water to remove trace of contaminants. The pH measurements were performed with a Metrohm pH-meter Model 827 with a combined glass electrode with the Ag/AgCl reference electrode filled with 3 mol·L⁻¹ NaCl solution. Centrifugation of the mixtures was carried out in a FANEM 206-R centrifuge. Agitation of the mixtures was performed on an Incubator Shaker Model AL-222-CF American Lab with controlled velocity and temperature (283, 298 and 313) K.

2.4. Adsorption and Desorption Experiments

The adsorption kinetics was investigated using the solution depletion method [23]. For kinetic studies, the solutions (samples and blanks) were prepared in 10.0 mL volumetric polyethylene flasks with screw caps. In stoppered plastic tubes, 0.1 g samples of coconut fiber were kept in contact with 10.0 mL of 5.5'-DI aqueous solutions $(1.91, 3.02 \text{ and } 4.02) \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ and were shaken for specific periods of time at different temperatures (283, 298 and 313) K. The supernatants were separated by centrifuging the mixtures and the concentration of 5.5'-DI was calculated by molecular absorption measurements at 612 nm (pH 2), with a 1-cm optical path cell. The adsorbed amount of 5.5'-DI at equilibrium was calculated by the difference (attenuation) in the absorbance of the aliquots drawn before and after shaking. The blank solution was prepared in the same way, but without 5.5'-DI solution.

For isotherm studies, 0.1 g samples of coconut fiber in stoppered polyethylene flasks with an aqueous solution (10.0 mL) of 5.5'-DI (0.40 to 5.01) × 10^{-5} mol·L⁻¹ at (283, 298 and 313) K were shaken separately for a specific period of time previously defined in the kinetic studies.

A similar experimental procedure was used to evaluate 5.5'-DI desorption from the loaded adsorbent. In plastic tubes 0.1 g of coconut fiber modified by 5.5'-DI adsorption was added NaOH $(10^{-3}, 10^{-2} \text{ and } 10^{-1}) \text{ mol} \cdot \text{L}^{-1}$ and the mixtures were shaken for specific periods of time (10 and 30 minutes), at controlled temperature 298 K and a constant shaking speed was kept. After the contact time, the supernatants were separated by centrifuging the mixtures and the concentration of 5.5'-DI was determined as previously described.

3. Results and Discussion

3.1. Spectral Characteristics and Analytical Curve of 5.5'-DI

The maximum absorbance wavelength was determined from the 5.5'-disulfonic (5.5'-DI) spectrum, 612 nm. The analytical curve for 5.5'-DI aqueous solutions in the concentration range of 4.01×10^{-6} to 5.01×10^{-5} mol·L⁻¹ at pH 2 was obtained, and the respective parameters were calculated using a least-squares method. The correlation coefficient, $r^2 = 0.9991$, reveals an excellent linear fit to the experimental data. The linear fit equation can be written as:

$$A^{612\,\text{nm}} = (1.96 \pm 0.01) \times 10^4 \times C_{55',\text{DI}} + (0.0077 \pm 0.0002) \tag{1}$$

3.2. Effect of the Contact Time

Several experiments were conducted to assess the necessary time to obtain the maximum adsorption of 5.5'-DI onto green coconut fiber. Figures 3(a)-(c) show the mass-time profiles $[q_t = (m_{5.5'-DI}/m_{fiber}) \text{ vs } t]$ for adsorption of initial concentrations (1.91, 3.02 and 4.02) × 10⁻⁵ mol·L⁻¹ onto the fiber at 283 K (3-a), 298 K (3-b) and 313 K (3-c) at pH 2.]

Maximum sorption of 5.5'-DI was achieved after 60 minutes for three concentrations and at all temperatures. The preliminary experiments showed that the adsorption of 5.5'-DI is fast at the initial stages and becomes slower near the equilibrium. At 283, 298 and 313 K the maximum sorption, $q_{\text{max,exp}}$, for the lowest initial concentration ($C_0 = 1.91 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$) of 5.5'-DI was (5.01, 5.24 and 6.14) $\times 10^{-4} \text{ g}\cdot\text{g}^{-1}$; for $C_0 = 3.02 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ (0.93, 1.01 and 1.03) $\times 10^{-3} \text{ g}\cdot\text{g}^{-1}$ and for $C_0 = 4.02 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ (1.32, 1.40 and 1.49) $\times 10^{-3} \text{ g}\cdot\text{g}^{-1}$, respectively. The rate of 5.5'-DI adsorption onto the fiber is very rapid during the initial 30 minutes and decreases thereafter, as can be seen from Figure 3.

It is revealed that there was no considerable adsorption for 5.5'-DI after 120 minutes. The time profile of 5.5'-DI uptake is a single, smooth, and continuous curve leading to saturation ($q_{\max,exp}$), suggesting a possible monolayer coverage of 5.5'-DI on the surface of the coconut fiber adsorbent [24]. The increase in the adsorption capacity at a higher temperature indicated the endothermic nature of the adsorption process of 5.5'-DI onto co-conut fiber. Similar results of adsorption of dyes onto different adsorbents with a positive change in entropy and enthalpy have been reported in literature [25]-[28].

3.3. Adsorption Kinetics

The kinetic adsorption study is essential to optimize the processes and ensure that significant adsorption of the 5.5'-DI occurred under different conditions. Furthermore, it is possible to determine the solute uptake rate that controls the residence time of the adsorbate at the solid-solution interface. Kinetic models were applied to interpret the experimental data in order to understand the mechanisms that control the adsorption process, such as the mass transfer in solution and the chemical interactions [29].

The first kinetic model used to fit the experimental data was that of Lagergren, Equation (2), which was the first equation developed to describe adsorption in liquid-solid systems based on the capacity of the solid [14] [15]:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_1 \left(q_{\max} - q_t \right) \tag{2}$$

where $k_1 (\min^{-1})$ is the rate constant of pseudo-first-order adsorption, $q_{\max, calc}$ is the maximum amount of 5.5'-DI



Figure 3. Dependence of adsorbed mass of 5.5'-DI per fiber unit mass on time of contact at pH 2. (a) 283 K; (b) 298 K; and (c) 313 K. \blacktriangle 4.02 × 10⁻⁵ mol·L⁻¹, \blacksquare 3.02 × 10⁻⁵ mol·L⁻¹ and \bullet 1.91 × 10⁻⁵ mol·L⁻¹.

adsorbed $(g_{5.5'-DI}/g_{fiber})$ (based on the adsorption capacity which corresponds to the monolayer coverage) and q_t is the amount of 5.5'-DI adsorbed on the fiber $(g_{5.5'-DI}/g_{fiber})$ when $t \neq 0$ and t_{max} (equilibrium time of solid-liquid system which corresponds to the maximum adsorption kinetics). Integrating Equation (2) considering the initial

conditions as $q_t = 0$ at t = 0 and the equilibrium condition $q_{ads} = q_t$ for each time t, becomes:

$$\log(q_{\max} - q_t) = \log q_{\max,\text{calc}} - \frac{k_1}{2.303}t \tag{3}$$

By applying the pseudo-first order model to the experimental values (Figures are not shown here) the slope and the intercept of each linear fit were used to calculate the first order rate constant (k_1) and the adsorption at equilibrium $(q_{\max,calc})$. The correlation coefficients (r^2) of the first order kinetic fit to the experimental conditions were not very good for all studied temperatures. Such behavior was observed throughout the contact time and initial concentration evaluated. Also, the values of $q_{\max,calc}$ were quite different from the values found in the experimental kinetic study $(q_{\max,exp})$. These results suggest that the adsorption of 5.5'-DI onto green coconut fiber does not follow a pseudo-first order model, indicating that 5.5'-DI does not adsorb onto material occupying one adsorption site.

The adsorption kinetics may also be described by a pseudo-second order equation introduced by Blanchard *et al.* [16] and reviewed by Ho and McKay [30]:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_2 \left(q_{\mathrm{max,cal}} - q_t \right)^2 \tag{4}$$

where k_2 is the pseudo-second order adsorption rate constant, $(\min^{-1} g_{\text{fiber}}/g_{5.5^{\circ}-\text{DI}})$, and $q_{\max,\text{calc}}$ and q_t have the same definitions as in Equation (3). Integrating Equation (4) and applying the same boundary conditions gives we can obtain:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{\text{max,calc}}^2} + \frac{1}{q_{\text{max,calc}}}t$$
(5)

The second-order rate constant (k_2) and the maximum amount of 5.5'-DI adsorbed ($q_{max,calc}$) may be calculated from the intercept and the slope of the linear relationship, Equation (5), between t/q_t and t. The curve fit was calculated by adjusting Equation (5) to the experimental data (Figures are not shown here). The parameters $q_{max,calc}$ and k_2 are shown in Table 2.

The correlation coefficients (r^2) for the pseudo-second order kinetic model fit are very good and the values of $q_{\text{max,calc}}$ (**Table 2**) are quite similar to those obtained from the kinetic experiment data ($q_{\text{max,exp}}$) at different temperatures (283, 298 and 313) K and initial concentrations of 5.5'-DI (1.91, 3.02 and 4.02) × 10⁻⁵ mol·L⁻¹. At 283 K, 298 K and 313 K the maximum sorption, $q_{\text{max,exp}}$, for the lowest initial concentration ($C_o = 1.91 \times 10^{-5}$ mol·L⁻¹) of 5.5'-DI were (5.01, 5.24 and 6.14) × 10⁻⁴ g·g⁻¹; for $C_o = 3.02 \times 10^{-5}$ mol·L⁻¹ (0.93, 1.01 and 1.03) × 10⁻³ g·g⁻¹ and for $C_o = 4.02 \times 10^{-5}$ mol·L⁻¹ (1.32, 1.40 and 1.49) × 10⁻³ g·g⁻¹, respectively. The pseudo-second order model fit suggests that the interaction of each molecule of dye with the fiber surface occurs by the occupation of two sites on the biomaterial. In the lowest initial concentration ($C_o = 1.91 \times 10^{-5}$ mol·L⁻¹), the large number of adsorption sites favored the adsorption and, consequently, k_2 presents a higher value for all temperatures studied 283 K (5.44 × 10² min⁻¹), 298 K (4.58 × 10² min⁻¹) and (5.79 × 10² min⁻¹). However, considering all 5.5'-DI initial concentrations, values of k_2 show an irregular variation. A minimum value was observed and as a result, k_2 tends to a constant value, irrespective of the initial concentration. Therefore, considering the whole time interval and 5.5'-DI concentrations, it can be assumed that the adsorption mechanism follows the pseudo-second order model. It was observed that the increase in values of the maximum amount of 5.5'-DI adsorbed, $q_{\text{max,calc}}$, for $C_o = (1.91, 3.02 \text{ and }4.02) \times 10^{-5} \text{ mol·L}^{-1}$ respectively with an increase in the temperature 283 K, 298 K and 313 K indicates a possible endothermic system. Similar behavior was seen in literature [31].

Table	Pseud	lo-second	order	parameters f	for th	e adsor	otion c	of 5.5	5'-DI o	nto fiber	at p	H 2.

	Pseudo-second-order parameters									
C_0 (mol·L ⁻¹)	$q_{ m max,c}$	$_{\rm alc} imes 10^4 ~(g_{5.5'-{ m DI}})$	$\times \ 10^4 \ (g_{5.5'\text{-DI}}/g_{fiber})$		$k_2 imes 10^{-2} ({ m min}^{-1} { m g_{fiber}}/{ m g_{5.5'-DI}})$			r^2		
	283 K	298 K	313 K	283 K	298 K	313 K	283 K	298 K	313 K	
$1.91\times10^{\text{-5}}$	(5.04 ± 0.01)	(5.52 ± 0.02)	(6.15 ± 0.01)	(5.44 ± 0.02)	(4.58 ± 0.02)	(5.79 ± 0.01)	0.9979	0.9908	0.9979	
$3.02\times 10^{\text{-5}}$	(0.95 ± 0.01)	(1.01 ± 0.01)	(1.03 ± 0.01)	(1.81 ± 0.01)	(2.67 ± 0.01)	(1.67 ± 0.01)	0.9975	0.9919	0.9985	
$4.02\times 10^{\text{-5}}$	(12.7±0.02)	(14.6±0.01)	(15.4±0.02)	(2.40±0.02)	(1.69±0.01)	(0.92±0.02)	0.9902	0.9936	0.9964	

Adsorption involves varied stages, where the rate controlling step is the intraparticle diffusion mechanism. Close to the equilibrium, the intraparticle diffusion becomes slower due to low concentration. Considering that pseudo-first order and -second models cannot identify the diffusion mechanisms, an intraparticle diffusion model [17] was also evaluated. The rate parameters for intraparticle diffusion (k_P) may be obtained by using Equation (6), where q_t is the amount of 5.5'-DI on coconut fiber at different times, t (min):

$$q_t = k_P^{1/2} + B \tag{6}$$

where k_P is the intraparticle diffusion rate constant (min^{-1/2} g_{5.5'-DI}/g_{fiber}). According to Equation (6), a plot of q_t versus $t^{1/2}$ should be a straight line with a slope corresponding to k_P when the intraparticle diffusion is a rate-limiting step and *B* is the intercept corresponding to the linear coefficient. Figures 4(a)-(c) shows the data for (1.91, 3.02 and 4.02) × 10⁻⁵ mol·L⁻¹ initial concentration of 5.5'-DI at 283 K (a), 298 K (b) and 313 K (c).

The intraparticle diffusion model could be applied to experimental data obtained in different initial concentrations (Figure 4). It was observed that nonlinear plots over the whole range of time (multilinearity) indicating that other processes drive the adsorption of 5.5'-DI on coconut fiber. In general, a first sharper portion of the curve may be considered as an external surface adsorption or a faster adsorption stage. A second portion is a gradual adsorption stage, where intraparticle diffusion is rate-controlled and an irregular variation of the diffusion rate with the initial 5.5'-DI concentration was observed. The third portion is attributed to the final equilibrium stage where the intraparticle diffusion is slower due to the extremely low adsorbate concentrations in solution.

The rate of uptake might be limited by size of adsorbate molecule, concentration of the adsorbate and its affinity to the adsorbent, diffusion coefficient of the adsorbate in the bulk phase, the pore-size distribution of the adsorbent and agitation rate. Values of k_P (min^{-1/2} g_{5.5'-DI}/g_{fiber}) and the correlation coefficients for all 5.5'-DI initial concentrations investigated are shown in **Table 3**. High correlation coefficient (r > 0.97) is found to the range of the experimental data to the diffusion model. The second portion of the curves can be attributed to intraparticle diffusion [32]-[34] and an irregular variation of the diffusion rate with initial 5.5'-DI concentration and temperature were observed.

An irregularity of the k_P values was also reported in literature [35] that can be related to either the heterogeneity of the material or the capability of adsorbate molecules to agglomerate on its surface. Intercept values of the linear diffusion segments, named as B, does not pass through the origin of the graphic plot indicating that intraparticle diffusion is not the single mechanism rate-controlling and other mechanisms may control the rate adsorption.

Validation requires the comparison of quantitative correlation coefficients, and they can be seen in the graphs of the linear equation used in its respective kinetic model [33]. Green coconut fiber has a high level of compression where most of the binding sites are not exposed to the substrate. However, certain solvents can swell (decompressing) the fiber, exposing more ligands within the cellulosic network for binding with the adsorbate [35]. For all temperatures it was observed that as the initial concentration increased (1.91, 3.02 and 4.02) $\times 10^{-5}$ mol·L⁻¹ the intraparticle diffusion constant increase too (Table 3).

3.4. Desorption Studies

To verify the possibility of using successively coconut fiber, the elution of 5.5'-DI adsorbed onto fiber was studied. The main objective was to evaluate how often the modified solid phase can be used without losing the initial properties of the same. In this experiment, it was evaluated the 5.5'-DI desorption of the fiber with NaOH solution $(10^{-3}, 10^{-2} \text{ and } 10^{-1}) \text{ mol·L}^{-1}$ in contact during 10 and 30 minutes at 298 K. The experiments were performed in duplicate and the results are shown Table 4.

Desorption percentage was estimated considering initial concentration $C_o = 4.02 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$, corresponding $q_{\text{max,exp}} = 1.40 \times 10^{-3} \text{ g} \cdot \text{g}^{-1}$ and $q_{\text{max,calc}} = 1.46 \times 10^{-3} \text{ g} \cdot \text{g}^{-1}$ at 298 K. According to the results shown in Table 4, the highest leaching was observed for $10^{-1} \text{ mol} \cdot \text{L}^{-1}$ NaOH during 30 minutes of contact. These differences are probably associated to the acid-base equilibria involved and neutralization of the acid. Desorption studies also contribute to selecting the suitable material to use in separation and preconcentration procedures.

3.5. Adsorption Isotherms

Figure 3 shows the plots of adsorption isotherms, $q_{\text{max,exp}}$ versus C_o, for 5.5'-DI adsorption by fiber at 283 K,



Figure 4. Intraparticle diffusion model for 5.5'-DI/fiber system at initial concentration and different temperatures: (a) 283 K; (b) 298 K; and (c) 313 K. \blacktriangle 4.02 × 10⁻⁵ mol·L⁻¹, \blacksquare 3.02 × 10⁻⁵ mol·L⁻¹ and \bullet 1.91 × 10⁻⁵ mol·L⁻¹.

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	Intraparticle diffusion parameters										
C_o (mol·L ⁻¹)	$k_p imes 10^5 ({ m min}^{-1/2} { m g}_{5.5'-{ m DI}}/{ m g}_{ m fiber})$			$m{B} imes 10^4$			r^2				
	283 K	298 K	313 K	283 K	298 K	313 K	283 K	298 K	313 K		
$1.91\times 10^{\text{-5}}$	(2.36 ± 0.01)	(2.41 ± 0.01)	(2.63 ± 0.02)	(1.27 ± 0.01)	(1.26 ± 0.01)	(2.87 ± 0.02)	0.9914	0.9929	0.9951		
$3.02\times 10^{^{-5}}$	(2.87 ± 0.02)	(4.21 ± 0.03)	(5.35 ± 0.01)	(2.67 ± 0.02)	(2.55 ± 0.03)	(5.40 ± 0.03)	0.9964	0.9857	0.9827		
4.02×10^{-5}	(5.20 ± 0.02)	(6.50 ± 0.01)	(7.49 ± 0.01)	(1.51 ± 0.02)	(1.99 ± 0.01)	(4.88 ± 0.01)	0.9916	0.9968	0.9911		

Table 3 Difusion intraparticle parameters for the adsorption of 5.5-DI solution onto fiber at pH 2

Table 4. Results of desorption studies of fiber modified with 5.5'-DI ($C_o = 4.02 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$).

	Desorption (%)				
NaOH (mol·L ⁻¹)	10 ⁻³	10 ⁻²	10 ⁻¹		
10 minutes	19	30	85		
	22	29	87		
30 minutes	24	47	100		
	27	50	100		

298 K and 313 K. It was indicated that 5.5'-DI adsorption capacity increased with a higher temperature. After determining the best conditions for the adsorption study, experimental data were obtained by varying the initial adsorbate by keeping a constant time of contact between the fiber and 5.5'-DI adsorbate. Isotherms show the relationship between adsorbate concentration in solution and the amount of adsorbate adsorbed onto a specific sorbent at a constant temperature [36] [37]. To understand the adsorption equilibrium, three commonly used mathematical models were compared with experimental data: the Langmuir [18], Freundlich [19] and Dubinin-Radushkevich [20] isotherms.

The Langmuir model [37] was originally developed to represent chemisorption on a set of well-defined andlocalized adsorption sites with the same adsorption energy, irrespective of the surface coverage and with no interaction between adsorbed molecules. Maximum sorption is defined when the adsorbent surface is covered with a monolayer of adsorbate, and each site is responsible for the adsorption of a single molecule of dye and no further adsorption may therefore occur [38] [39]. The model allows applying experimental data in an extensive range of concentration [40]. The familiar form of Langmuir isotherm, based on these kinetic considerations, is expressed as Equation (7) that describes a nonlinear form, which relates the adsorbed mass m_{ads} (g·g⁻¹) and the equilibrium concentration C_{eq} (g·L⁻¹).

$$m_{ads} = \frac{m_{ads}^{\max} K_L C_{eq}}{1 + K_L C_{eq}}$$
(7)

where m_{ads} is the amount of 5.5'-DI adsorbed on the fiber (g·g⁻¹), m_{ads}^{max} is the maximum amount of solute adsorbed (g) per gram of fiber (adsorption capacity), C_{eq} is the equilibrium concentration of 5.5'-DI in solution (g·L⁻¹) and K_L is the Langmuir constant (L·g⁻¹), which is related to the equilibrium constant of the adsorption process, including physical, chemical and energetic characteristics. The linear Equation (8) is obtained by rearrangement of Equation (7):

$$\frac{1}{m_{ads}} = \frac{1}{m_{ads}^{\max} \times K_L \times C_{eq}} + \frac{1}{m_{ads}^{\max}}$$
(8)

The empirical parameters were then obtained by using a dye concentration ranging from $(3.01 \times 10^{-6} \text{ to } 4.70 \times 10^{-5}) \text{ mol}\cdot\text{L}^{-1}$ at pH 2 and at (283, 298 and 313) K. The curve fit was calculated by adjusting Equation (8) to the experimental data with Origin 8.1 software (Figures are not shown here). Table 5 shows the results of applying the Langmuir isotherm by the minimum square method. The fit of these linear curves resulted in correlation coefficients of 0.9929, 0.9902 and 0.9951, respectively, for 283 K, 298 K and 313 K. Values of K_L are (61.4 $\text{L}\cdot\text{g}^{-1}$ at 283 K), (78.4 $\text{L}\cdot\text{g}^{-1}$ at 298 K) and (98.8 $\text{L}\cdot\text{g}^{-1}$ at 313 K).

Isotherm model		Temperature (K)	
Langmuir	283	298	313
$K_L \left(\mathrm{L} \cdot \mathrm{g}^{-1} ight)$	61.4 ± 0.1	78.4 ± 0.2	98.8 ± 0.2
m_{ads}^{\max} (g·g ⁻¹)	$(1.29\pm 0.02)\times 10^{-2}$	$(1.49\pm 0.01)\times 10^{-2}$	$(1.89\pm 0.01)\times 10^{-2}$
r^2	0.9929	0.9902	0.9951
RMD (%)	11	12	11
Freundlich			
$K_F\left(\mathbf{g}\cdot\mathbf{g}^{-1} ight)$	30.6 ± 0.2	136.5 ± 0.1	22.1 ± 0.2
n	0.73 ± 0.01	0.52 ± 0.03	0.50 ± 0.01
r^2	0.9959	0.9927	0.9963
RMD (%)	3.7	4.5	4.9
Dubinin-Radushkevich			
$K_{DR} (\mathrm{mol} \cdot \mathrm{g}^{-1})$	23.9 ± 0.1	18.2 ± 0.2	27.5 ± 0.1
$B (\mathrm{mol}^2 \cdot \mathrm{J}^{-2})$	$(2.63\pm 0.01)\times 10^{-8}$	$(1.28\pm 0.02)\times 10^{-8}$	$(2.22\pm 0.02)\times 10^{-8}$
$E (kJ \cdot mol^{-1})$	4.36	6.26	4.75
r^2	0.9915	0.9918	0.9997
RMD (%)	6.9	7.1	4.6

Table 5. Parameters of Langmuir, Freundlich and Dubinin-Radushkevich models for adsorption of 5.5'-DI on coconut fiber.

The maximum amount of solute adsorbed (g) per gram of fiber is $1.29 \times 10^{-2} \text{ g} \cdot \text{g}^{-1}$ (283 K), $1.49 \times 10^{-2} \text{ g} \cdot \text{g}^{-1}$ (298 K) and $1.89 \times 10^{-2} \text{ g} \cdot \text{g}^{-1}$ (313 K). The Langmuir parameters described in **Table 5** indicate that the adsorption capacity for the 5.5'-DI/fiber system is more favorable at high temperatures. Furthermore, this may be correlated with the higher surface area and lower pore size for fiber (**Table 1**) which present an important effect on the adsorption capacity. The K_L contants indicate higher bonding energy of 5.5'-DI on fiber at 313 K than at 283 K. While the Langmuir isotherm assumes that the enthalpy of adsorption is independent of the amount adsorbed, the Freundlich isotherm is derived assuming a logarithmic decrease in the enthalpy of adsorption with the increase in the fraction of occupied sites.

The Freundlich isotherm [32], one of the most widely used mathematical descriptions, usually fits the experimental data over a wide range of concentrations. This isotherm gives an empirical expression that encompasses the surface heterogeneity and the exponential distribution of active sites and their energies [33]. The Freundlich adsorption isotherm does not predict any saturation of the solid adsorbent surface; thus, infinite surface coverage is mathematically feasible. The Freundlich model is shown in Equation (9):

$$n_{ads} = K_F C_{eq}^{1/2} \tag{9}$$

where m_{ads} and C_{eq} have the same definitions previously presented for the Langmuir isotherm, K_F (g·g⁻¹) is an empirical constant which provides an indication of the adsorption capacity of adsorbent, and 1/n indicates the energetic heterogeneity of adsorption sites. Equation (9) can be manipulated to give the following linear equation, Equation (10):

$$\log m_{ads} = \log K_F + \frac{1}{n} \log C_{eq} \tag{10}$$

The plots of $\log m_{ads}$ vs $\log C_{eq}$ are shown in **Figures 5(a)-(c)** at different temperatures (283, 298 and 313) K. The constants 1/n and K_F were determined from the slope and the intercept of the plots.

The high correlations ($r^2 = 0.9959$, 0.9927 and 0.9963 for 283 K, 298 K and 313 K, respectively) show that the model is very suitable for describing the adsorption systems in the concentrations ranges, thus K_F and n values shown on **Table 5**. The values of n obtained from the adsorption of 5.5'-DI at all temperatures (283 K, 298 K and 313 K) were less than 1 (0.73, 0.52 and 0.50, respectively), indicating that adsorption is thermodynamically favored and the sites have a narrow energy distribution. At n = 1, all sites are energetically homogenous, and the model reduces to the Langmuir isotherm, where the adsorbed mass is a direct function of the equilibrium



Figure 5. Adsorption isotherms of the 5.5'-DI/fiber system at different temperatures: (a) 283 K; (b) 298 K; and (c) 313 K and pH 2. Solid line corresponds to the Freundlich model fitting.

concentration. When n > 1, high energy sites exist and are the first to be occupied. The higher the value of n, the more energetically heterogeneous the adsorption sites.

The Freundlich adsorption isotherm does not predict any saturation of the solid adsorbent surface, therefore the infinite coverage is predicted mathematically [37]. Adsorption on fiber shows a K_F value (136.5 g·g⁻¹ at 298 K) higher than the corresponding K_F values (30.6 g·g⁻¹ at 283 K) and (22.1 g·g⁻¹ at 313 K) which represents a stronger interaction between 5.5'-DI and coconut fiber at 298 K.

To distinguish between physical and chemical adsorption, the Dubinin-Radushkevich [41] isotherm model was applied to the data. This model examines the heterogeneity of the energies at the surface. The Dubinin-Radushkevich model is shown in Equation (11):

$$\ln C_{ads} = \ln K_{DR} - B\varepsilon^2 \tag{11}$$

where C_{ads} is the amount of 5.5'-DI adsorbed per unit mass of the fiber (mol·L⁻¹·g⁻¹), K_{DR} is the maximum amount of 5.5'-DI adsorbed, C_{eq} have the same definitions as in the Langmuir isotherm (mol·L⁻¹), *B* is a constant with dimensions of energy; ε is the Polanyi potential (ε) = $RT \ln \left[1 + \left(\frac{1}{C_{eq}}\right)\right]$, where *R* is a gas constant (8.314 J·K⁻¹·mol⁻¹) and *T* is the temperature in Kelvin (K). This model is based on the theory of the Polanyi potential sorption that assumes a fixed volume of sorption space close to the adsorbent and the existence of sorption potential over these spaces [42] [43].

According to Antonio *et al.* [37], if the surface is heterogeneous and a Langmuir isotherm approximation is chosen as a local isotherm for all energetically equivalent sites then the quantity $B^{1/2}$ can be related to the mean sorption energy (*E*) according to:

$$E = \frac{1}{\sqrt{-2B}} \tag{12}$$

where *E* is the free energy equivalent to the transfer of 1 mol of solute from infinity to the surface of the fiber. A linear plot of $\ln C_{ads}$ versus ε^2 (Figure 6) yielded linear regression coefficients of ($r^2 = 0.9915$, 0.9918 and 0.9997 for 283 K, 298 K and 313 K, respectively).

The calculated values (**Table 5**) of *B* and K_{DR} from the slope and intercept are $(-2.63 \times 10^{-8} \text{ J}^2 \cdot \text{mol}^{-2})$ and 23.9 mol·g⁻¹ at 283 K, $(-1.28 \times 10^{-8} \text{ J}^2 \cdot \text{mol}^{-2})$ and 18.2 mol·g⁻¹ at 298 K, $(-2.22 \times 10^{-8} \text{ J}^2 \cdot \text{mol}^{-2})$ and 27.5 mol·g⁻¹ at 313 K. The numerical values of *E* calculated from Equation (12) are 4.36 kJ·mol⁻¹ (283 K), 6.26 kJ·mol⁻¹ (298 K) and 4.75 kJ·mol⁻¹ (313 K). As can be seen in **Table 5**, the numerical values of *E* as calculated from Equation (12) demonstrate a purely physical adsorption of 5.5'-DI on coconut fiber because they are smaller than 50 kJ·mol⁻¹ [29]. This type of adsorption involves weaker binding energies (van der Waals) which are usually between 8 and 25 kJ·mol⁻¹ [36].

3.6. Evaluation of the Fit Quality

The isotherm parameters were determined by nonlinear regression [44] [45] using Origin 8.1 software. The quality of fit was assessed using the coefficient of determination (r^2) and average relative error (*RMD*) according to Equation (13):

$$RMD(\%) = \frac{100}{n} \sum_{n=1}^{n} \frac{|q_{exp} - q_{mod}|}{q_{mod}}$$
(13)

where q_{exp} and q_{mod} are, respectively, the experimental values and the values estimated by the model. Table 5 shows the *RMD* for all the isotherm models at each temperature.

For all the temperatures studied, it was observed that the Freundlich model is the best to describe the 5.5'-DI adsorption isotherm in green coconut fiber ($r^2 > 0.9927$ and RMD < 5.0). These values demonstrate the presence of energetically homogeneous adsorption sites of the adsorbent tested in which a reversible adsorption process occurs.

Thus, it is assumed that an increase in the adsorbate concentration causes an increase in the amount adsorbed on the adsorbent surface. Theoretically, using this isotherm, an infinite amount of adsorption can occur [46].

3.7. Thermodynamic Study

Thermodynamic parameters that provide in-depth information on the inherent energetic changes associated with



Figure 6. Adsorption isotherms of 5.5'-DI/fiber system at different temperatures: (a) 283 K; (b) 298 K; and (c) 313 K and pH 2. Solid line corresponds to the Dubinin-Radushkevich model fitting.

the adsorption process were accurately evaluated [32]. From the experimental data (varying temperatures and the concentration of 5.5'-DI) the enthalpy (ΔH^o), entropy (ΔS^o) and Gibbs free energy (ΔG^o) were determined. The Gibbs free energy was calculated using Equation (14):

$$\Delta G^o = -RT \ln K_L \tag{14}$$

where K_L , R and T were previously defined. The Gibbs free energy can also be expressed by Equation (15):

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \tag{15}$$

Substituting Equation (14) into Equation (15), Equation (16) is obtained and through it ΔH^o and ΔS^o are calculated:

$$\ln K_L = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R}$$
(16)

Both ΔH^o and ΔS^o were determined from the slope and intercept of van't Hoff plots of $\ln K_L$ versus 1/T. The results of the fit to experimental data give values for the thermodynamic parameters of ΔH^o and ΔS^o . The positive value of ΔH^o (+11.6 kJ·mol⁻¹) confirms that the adsorption is endothermic process, and the value of ΔS^o (+75.5 J·mol⁻¹·K⁻¹) suggests the increased randomness at the solid/liquid interface during the adsorption process so that increased entropy induces the replacement of ionic dye for water molecules around adsorbent particle.

The ΔG° values were negative at all temperatures -9.7 kJ·mol⁻¹ at 283 K, -10.8 kJ·mol⁻¹ at 298 K and -11.9 kJ·mol⁻¹ at 313 K, what corroborate that the adsorption of dyes onto coconut fiber was both spontaneous and thermodynamically favored. Furthermore, the decrease in the value of ΔG° with a rise in temperature indicates that the adsorption is more spontaneous at higher temperatures. Similar behavior was seen in literature [35].

4. Conclusions

Green coconut fiber showed considerable potential low cost adsorbent for its use in the adsorption of 5.5'-DI from aqueous solution. The adsorbent had good adsorption capacity for 5.5'-DI and showed strong adsorption as the initial concentration of the 5.5'-DI was increased. The kinetic study demonstrated that the equilibrium time of contact was about 30 minutes for both temperatures and dye initial concentration. The pseudo-second order adsorption model adequately represents the interaction of 5.5'-DI with coconut fiber, showing that adsorption occurs by the occupation of two active sites on the surface of the bio(adsorbent) as reported in literature [47] [48]. Adsorption parameters calculated from Langmuir, Freundlich and Dubinin-Radushkevich isotherms are useful for the explanation of the mechanisms of the adsorption process as indicated by the good linear correlation coefficient values. The values of the mean sorption energy (*E*) at different temperatures all characterize a physical rather than chemical adsorption. For all temperatures studied, the Freundlich is the model that best describes the adsorption isotherm of 5.5'-DI onto green coconut husk fiber ($r^2 > 0.9927$ and RMD < 5.0). Thermodynamic studies show the adsorption process to be endothermic and spontaneous.

Considering adsorption, desorption, kinetic modeling and physical properties of the adsorbent, coconut fiber is an appropriate material in future analytical applications.

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