Kinetic Modeling of Adsorption of Indigo Carmine (5, 5'-Disulfonic Indigotin) on Peat

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Abstract: *The kinetic of Indigo Carmine (5,5'- disulfonic indigotin, 5,5'-DI) adsorption on fibrous peat (FP) and decomposed peat (DP), have been investigated at different temperatures (283, 298, 313) K at pH 2. The effect of particle size was studied considering the variation of grain size of each peat (2000-850, 850-600 and < 600) nm. The fibrous peat shows higher adsorption capacity than the decomposed peat, while under the same work conditions. The kinetics of adsorption of 5,5'-DI is discussed using three kinetic models, the first-order Lagergren model, the pseudo-second-order model, and the intraparticle diffusion model. The adsorption of 5, 5'-DI onto peat proceeds according to the pseudo second-order model and the correlation coefficients were very close to 1. At 283, 298 and 313 K the maximum sorption, $q_{max,calc}$, for the initial concentration ($C_o = 4.05 \times 10^{-5}$ mol L^{-1}) of 5,5´-DI were $q_{max,calc}$ is (5.57, 7.92 e 8.29) $\times 10^{-4}$ g g^{-1} for fibrous peat and (5.29, 6.74 e 5.83) $\times 10^{-4}$ g g^{-1} for decomposed peat. The intraparticle diffusion of 5,5'-DI molecules within the peat particles was identified as the rate-limiting step.*

Keywords: *Adsorption, peat, kinetic modeling, indigo carmine, spectrophotometry.*

1. INTRODUCTION

A number of materials have been used for solid–liquid extraction [1-3], such as polyurethane foam [4], polymeric resins [5-7], modified silica gel [8-10] and active carbon [11]. Some biological materials and products derived from industrial and agricultural activities have been also used as adsorbents for metals and other substances, mainly aiming remediation of contaminated water [12,13]. Rice [14], grape husks [15], sugarcane bagasse [16], bamboo charcoal [17] and microorganisms [18] were used as alternative solid-phases in the development of analytical methods for dye determination. Taking into account these characteristics, peat stands for a natural adsorbent for water remediation and analytical applications. Peat is an organic sediment formed from the partial decomposition of vegetable material in an environment moist, acid and low oxygenation [20-22]. Peat *in situ* generally contains 90% or more of water and when collected and air-dried to this level approaches 40% [23]. With regard to their appearance, peat presents a variable coloration between dark brown and black, soft consistency when wet and tenacious when dry [24]. From the point of physicochemical view, is a porous, highly polar, with high adsorption capacity for transition metals and polar organic molecule, Figure 1 [25].
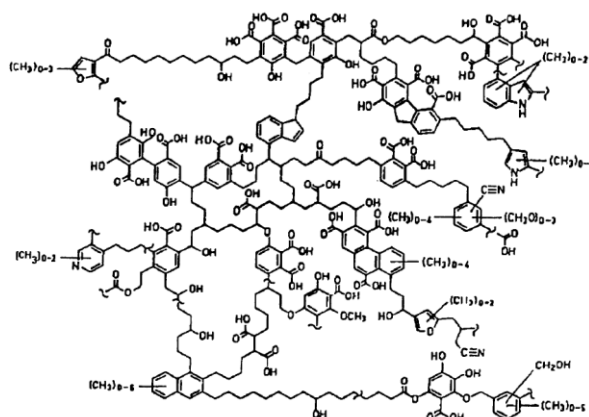

Figure1. *Molecular structure of humic acid ($C_{187}H_{186}O_{89}N_9S$)*

Peat is constituted by lignin, cellulose and humicsubstances (HS) [27], thus containing functional groups like carboxylic acids and phenolic or alcoholic hydroxyls benefiting the adsorption of organic molecules and complexation of metallic ions [28]. It is an organic sediment formed by partial decomposition of vegetal matter in acid and humid media, containing low-oxygen amounts. In the last thirty years, the peat has been much studied, primarily in Canada, the US and Europe, as alternative technology of using a natural adsorber [29-31]. Low cost, applied to the treatment of water and effluents contaminated by heavy metals and other toxics substances. In Brazil, this material has its application directed to agriculture or as combustible material, given its high content of carbon,Table 1.

Table1. *Brazilian regions with higher amounts of peat [30]*

Brazilian regions	Peat amount in tons (billion)
Amazon	6
South	500
Northest	42

However, few studies have been published concerning the use of national peat applied to the treatment contaminated water and wastewater [31,32]. This peat can be used in the preparation of composites such as bioplastics, natural adsorbent and as a source of raw materials for several processes [33]. 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 peat as the adsorbent [34]. This study aims to use peat as a (bio)adsorbent for retention of the organic compound 5,5'-disulfonic indigotin (C.I. 73015), [35-40]. Three simplified kinetic models including pseudo-first-and -second-order [41-43] equations and the intraparticle diffusion [44,45] were used to describe the adsorption processes.
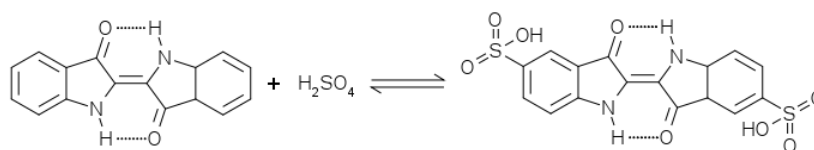
Figure2. *Reaction of indigo carmine (5,5'- disulfonic indigotin) [46]*

2. EXPERIMENTAL

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 [47-50]. 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 (573 and 576) K. 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 H_2SO_4 while stirring. The sulphonated species are obtained according to the chemical reaction (Fig.2). The temperature was kept at 353K and after cooling, the solution was diluted to 1000 mL with deionized water [35].

2.2. 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) HNO_3 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.

2.3. Biosorbent Material Preparation

The physico-chemical point of view, peat may be defined as a porous and highly and polar material, with high adsorption capacity and exchange cations [34]. The characteristics are directly influenced

by their age, by climate region where it formed the bog and mainly by the type of plant that originated (grasses, trees, mosses and other bog plants) [35]. Two types of peat from Santa Catarina, Brazil, were used being a decomposed type, ie it presents some degree of humidification and another of the fibrous type, with minimal or no degree of decomposition, Table 2. The fibrous and decomposed peats were washed with deionized water and after it was dried at 313K for 24 hours. It was adopted to work with different granulometries: (850 to 2000) mm, (850 to 600) mm and less than 600 mm.

Table2. *Physicochemical properties of fibrous peat and decomposed peat [27, 28]*

| Physicochemical Property	Fibrous peat (FP)	Decomposed Peat (DP)
Colour	light brown	dark brown
pH	2.18	3.98
Moisture content	56,30	67.78
Ash content	19,00	11.8

2.4. Adsorption Experiments

From the stock solution in an acid medium Indigo Blue (3.82×10^{-3} mol L^{-1}) were prepared 10.0 ml of solutions of different concentrations (0.49, 0.99, 2.00, 2.99, 4.00 and 4.76) $\times 10^{-5}$ mol L^{-1} at pH 2. Absorption spectra were recorded with maximum at 609 and 612 nm using a Shimadzu UV-2600 spectrophotometer quartz cuvette and optical path 1.00 cm. The analytical dye curves were constructed with the wavelengths chosen. The adsorption kinetics were investigated using the solution depletion method [35]. 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 peat were kept in contact with 10.0 mL of 5,5'-DI aqueous solutions (2.00, 2.99 and 4.00) $\times 10^{-5}$ mol L^{-1} at pH 2. The system was kept under constant orbital stirring of 150 rpm (American lab, Model LA-222 SC) and were shaken for specific periods of time at different temperatures (283, 298 and 313) K. Different contact times (5, 10, 15, 20, 30, 40, 60 and 120) minutes were studied. The supernatants were separated by centrifuging (Fanem®, Model 208N) the mixtures and the concentration of 5,5´-DI was calculated by molecular absorption measurements at 609 and 612nm (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.

3. RESULTS AND DISCUSSIONS

3.1. Spectral Characteristics and Analytical Curve of 5,5´-Di

The maximum absorbance wavelength was determined from the 5, 5'-disulfonic indigotin (5, 5´-DI) spectrum, 609 and 612 nm, Fig. 3. The analytical curve for 5, 5´-DI aqueous solutions in the concentration range of 4.90×10^{-6} to 4.76×10^{-5} mol L^{-1} at pH2 were obtained and the respective parameters were calculated using a least-squares method. The correlation coefficients, $r^2 = 0.9970$ (609 nm) and 0.9984 (612 nm), reveals an excellent linear fit to the experimental data. The linear fit equations can be written as eq.(1) and eq.(2):
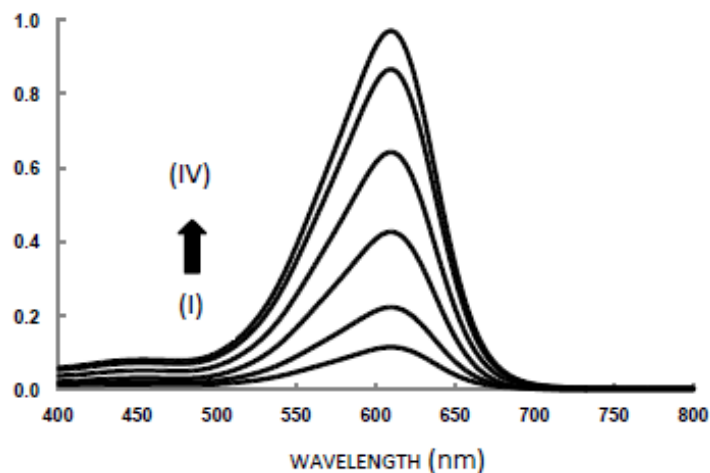
Figure3. *Spectrum of indigo carmine (5,5'- disulfonic indigotin) at pH 2, [5,5´-DI] = (I) 0.49 × 10^{-5}, (II) 0.99 × 10^{-5}, (III) 2.00 × 10^{-5}, (IV) 2.99 × 10^{-5}, (V) 4.00 × 10^{-5} e (VI) 4.76 × 10^{-5} (mol L^{1}).*

$$A^{609nm} = (2.05 \pm 0.01) \times 10^4 \times C_{5,5\text{-}DI} + (0.0200 \pm 0.0001) \qquad (1)$$

$$A^{612nm} = (2.01 \pm 0.02) \times 10^4 \times C_{5,5\text{-}DI} + (0.0222 \pm 0.0002) \qquad (2)$$

3.2. Effect of Contact Time and Particle Size

Several experiments were conducted to assess the necessary time to obtain the maximum adsorption of 5,5´-DI onto peats. The variation of grain size of peats (2000-850, 850-600 and less than 600) mm was studied in order to determine the influence of the adsorption of the 5,5´-DI at pH 2 and 298K. Considering the initial concentration of the dye solution 4.00×10^{-5} mol L^{-1}, FP/5,5´-DI and DP/5,5´-DI systems were placed at different contact times (5, 10, 15, 20, 30, 40, 60 and 120) minutes at 298 K. Tables 3 and 4 show the adsorbed mass of adsorbate values per gram of adsorbents as a function of the particle size of the solid phase, for contact times (30, 60, 120) minutes at wavelengths of 609 and 612 nm, respectively.

Table3. *Mass–time profiles [qt = ($m_{5,5\text{-}DI}$/ m_{peat}) vs. t] for adsorption of initial concentration 4.00×10^{-5} mol L^{-1} onto fibrous peat (FP) and decomposed peat (DP) at 298 K, 609 nm and 298K.*

Granulometry (mm)	($m_{5,5\text{-}DI}$/ m_{peat}) $\times 10^4$ (g g^{-1})					
	FP	DP	FP	DP	FP	DP
2000 - 850	1.08±0.01	1.82±0.01	1.89±0.02	2.16±0.01	3.19±0,03	2.82±0,02
850 - 600	2.62±0.02	2.50±0.01	3.59±0.03	3.20±0.01	4.95±0,01	3.90±0.01
less than 600	3.54±0.01	4.91±0.01	6.95±0.02	4.79±0.01	7.09±0,01	5.76±0.02
Contact time (min)	30		60		120	

Table4. *Mass–time profiles [qt= ($m_{5,5\text{-}DI}$/ m_{peat}) vs. t] for adsorption of initial concentration 4.00×10^{-5} mol L^{-1} onto fibrous peat (FP) and decomposed peat (DP) at 298 K, 612 nm and 298K.*

| Granulometry (mm)	($m_{5,5\text{-}DI}$/ m_{peat}) $\times 10^4$ (g g^{-1})					
	FP	DP	FP	DP	FP	DP
2000 - 850	1.10±0.03	1.83±0.02	1.90±0.01	2.18±0.03	3.21±0.01	2.85±0.02
850 - 600	2.64±0.01	2.53±0.03	3.63±0.02	3.22±0.02	5.01±0.01	3.95±0.01
less than 600	3.59±0.01	4.97±0.02	7.02±0.01	4.84±0.01	7.17±0.01	5.82±0.01
Contact time (min)	30		60		120	

It was observed that the adsorptive capacity of the two adsorbents studied increases the smaller the particle size. The reduction of the solid phase of particle size causes an increase in the contact surface between adsorbent and adsorbate, because of reduced resistance to mass transfer within the particles [52]. Thus, it adopted work with particle size less than 600 mm. Moreover, it observed also that the dye adsorbed mass per gram of peat values were very similar for the different wavelengths studied. Thus, the subsequent results were presented on 612 nm.

3.3. Effect of Temperature

Previous work [35] has shown the study about the adsorption of 5,5´-DI onto green coconut fiber (*Cocos Nucifera L*). Successive spectra (not presented here) of aliquots of the supernatant solutions obtained after the contact between FP and DP and (2.00, 2.99 and 4.05) $\times 10^{-5}$ mol L^{-1} dye solution at different time-periods, at (283, 298, 313) K, were registered. The increasing contact-time led to decreasing in the absorbances at 612 nm (pH 2). This variation in the absorbance may be described to the adsorption of 5,5´-DI on the fibrous and decomposed peats surface causing the decrease in the concentration of 5,5´-DI in the supernatant solutions. The Fig. 4 show the mass-time profiles ($q_t = m_{5,5\text{-}DI\ ads}/m_{peat}$ vs t) for adsorption of dye on fibrous peat (FP) and decomposed peat (DP). The minimum absorbance (maximum sorption) was achieved before 1 hour at (283, 298, 313) K for two types of peat. The maximum sorption, q_{max}, of 5,5´-DI per gram of FP is 7.17×10^4 (g g^{-1}) and for DP is 5.82×10^{-4} (g g^{-1}) at 298K, Table 5. The time profile of 5,5´-DI uptake is a single, smooth, and continuous curve leading to saturation, suggesting the possible monolayer coverage of 5,5´-DI on the surfaces of FP and DP adsorbents. In the same work [8], it was shown that the isotherm data could be well fitted by the Langmuir equation. It is well recognized that the characteristic of adsorbent surface is a critical factor that affects the sorption rate parameters and the film resistance plays an important role in the overall transport of the solute. The large number and array of different groups on fibrous peat (FP) and decomposed peat (DP) surfaces imply that there are different types of adsorbent-solute interactions. The increase in the adsorption capacity at a higher temperature indicated the endothermic

nature of the adsorption process of 5, 5´-DI onto peat. Similar results of adsorption of dyes onto different adsorbents with a positive change in entropy and enthalpy have been reported in literature [53-56].
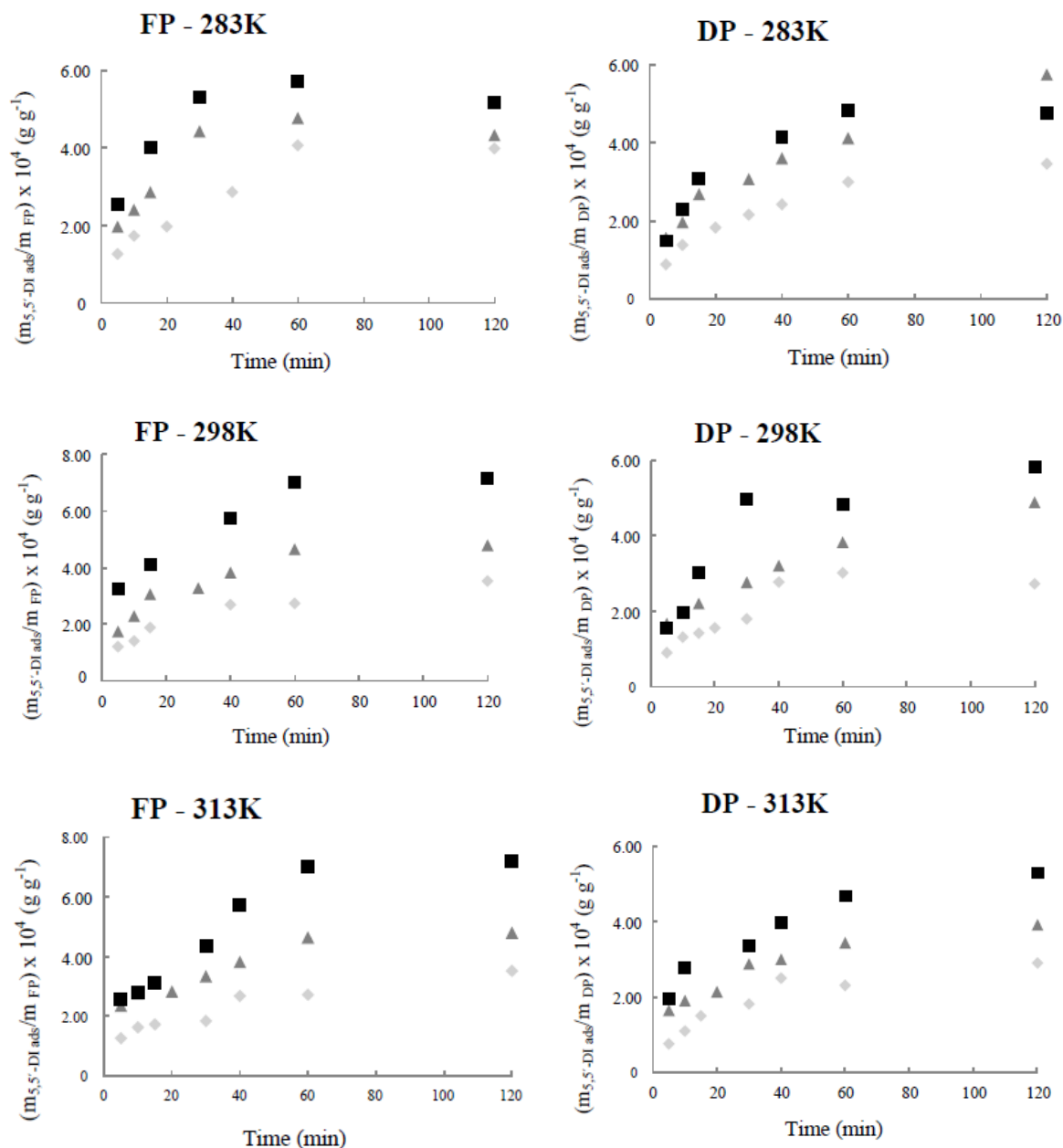
Figure4. *Mass-time profiles ($q_t = m_{5,5´-DI\ ads}/m_{peat}$ vs t) for adsorption of dye on fibrous peat (FP) and decomposed peat (DP) at (283, 298 e 313)K. [5,5´-DI] initial = ($\diamond$ 2.00, $\triangle$ 2.99 and $\blacksquare$ 4.00) × 10^{-5} mol L^{-1}, 612 nm.*

Table5. *Mass variation 5, 5´-DI adsorbed per gram of FP and DP as a function of contact time at different temperatures (283, 298 e 313) K, C_o = [5, 5´-DI] initial = (2.00, 2.99 and 4.00) × 10^{-5} mol L^{-1}, 612 nm.*

C_o (mol L^{-1})	T(K)	$(m_{5,5´-DI}/m_{FP}) \times 10^4$ (g g^{-1})	$(m_{5,5´-DI}/m_{DP}) \times 10^4$ (g g^{-1})
	283	3.99±0.02	3.45±0.04
2.00 × 10^{-5}	298	3.54±0.01	2.73±0.02
	313	3.54±0.01	2.88±0.03
	283	4.34±0.01	5.73±0.01
2.99 × 10^{-5}	298	4.80±0.02	4.88±0.01
	313	4.81±0.03	3.90±0.02
	283	5.19±0.01	4.74±0.01
4.00 × 10^{-5}	298	7.17±0.01	5.82±0.01
	313	7.19±0.02	5.27±0.01

3.4. 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 [8]. The first kinetic model used to fit the experimental data was that of Lagergren, eq.(3), which was the first equation developed to describe adsorption in liquid-solid systems based on the capacity of the solid [57,58]:

$$\frac{dq_t}{dt} = k_1 \left(q_{max,calc} - q_t \right)$$

(3)

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 adsorbed (g$_{5,5´-DI}$ /g$_{peat}$) (based on the adsorption capacity which corresponds to the monolayer coverage) and q_t is the amount of 5,5´-DI adsorbed on the peat (g$_{5,5´-DI}$ / g$_{peat}$) when $t \neq 0$ and t_{max} (equilibrium time of solid-liquid system which corresponds to the maximum adsorption kinetics). Integrating eq.(3) considering the initial conditions as $q_t = 0$ at $t = 0$ and the equilibrium condition $q_{ads} = q_t$ for each time t, becomes:

$$\log \left(q_{max} - q_t \right) = \log q_{max,calc} - \frac{k_1}{2,303} \times t$$

(4)

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 peat 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. [59] and reviewed by Ho and McKay [42]:

$$\frac{dq_t}{dt} = k_2 \times \left(q_{max,calc} - q_t \right)^2$$

(5)

Table6. *Pseudo-second order parameters for the adsorption of 5,5´-DI onto fibrous peat (FP) and decomposed peat (DP), C_o (initial concentration), k_2 (min^{-1} g$_{FP}$ g^{-1}$_{5,5´-DI}$) and $q_{max, calc}$ (g $_{5,5´-DI}$ g^{-1}$_{FP}$).*

C_o (mol L^{-1})	T (K)	FIBROUS PEAT (FP)			DECOMPOSED PEAT (DP)		
		$k_2 \times 10^3$	$q_{max, calc} \times 10^4$	r^2	$k_2 \times 10^3$	$q_{max, calc} \times 10^4$	r^2
2.00 × 10^{-5}	283	0.18±0.01	(4.50±0,01)	0.9939	0.10±0,02	4.11±0,01	0.9908
	298	0.16±0.01	(3.90±0,02)	0.9871	0.20±0,01	3.07±0,02	0.9933
	313	0.16±0.02	(3.86±0,01)	0.9848	0.14±0,01	3.38±0,01	0.9927
2.99 × 10^{-5}	283	0.24±0.01	(4.66±0,01)	0.9985	0.05±0,02	6.81±0,05	0.9910
	298	0.16±0.01	(5.24±0,02)	0.9984	0.09±0,03	5.48±0,03	0.9777
	313	0.16±0.02	(5.44±0,03)	0.9901	0.21±0,01	4.18±0,01	0.9933
4.00 × 10^{-5}	283	0.36±0.01	(5.57±0,01)	0.9901	0.17±0,01	5.29±0,01	0.9957
	298	0.11±0.01	(7.92±0,02)	0.9932	0.07±0,01	6.74±0,01	0.9950
	313	0.07±0.03	(8.29±0,02)	0.9845	0.12±0,02	5.83±0,01	0.9920

Where k_2 is the pseudo-second order adsorption rate constant, (min^{-1}g$_{peat}$/g$_{5,5´-DI}$), and $q_{max,calc}$ and q_t have the same definitions as in eq.(4). Integrating eq. (5) and applying the same boundary conditions gives we can obtain:

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

(6)

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, eq.(6), between t/q_t and t. The curve fit was calculated by adjusting eq. (6) to the experimental data (Figures are not shown here). The parameters $q_{max,calc}$ and k_2 are shown in Table 6.

The correlation coefficients (r^2) for the pseudo-second order kinetic model fit are very good and the values of $q_{max,calc}$ (Table 6) are quite similar to those obtained from the kinetic experiment data ($q_{max,exp}$) at different temperatures (283, 298 and 313) K and initial concentrations of 5,5´-DI (2.00, 2.99 and 4.00) $\times 10^{-5}$ mol L^{-1}, both for fibrous and decomposed peats. At 283 K, 298 K and 313 K, for FP the maximum sorption, $q_{max,exp}$, for the lowest initial concentration (C$_o$ = 2.00 $\times 10^{-5}$ mol L^{-1}) of 5.5´-DI were (4.50, 3.90 and 3.86) $\times 10^{-4}$ g g^{-1}; for C$_o$ = 2.99 $\times 10^{-5}$ mol L^{-1} (4.66, 5.24 and 5.44) $\times 10^{-4}$ g g^{-1} and for C$_o$ = 4.00 $\times 10^{-5}$ mol L^{-1} (5.57, 7.92 and 8.29) $\times 10^{-4}$ g g^{-1}, respectively. And for decomposed peat (DP) the maximum sorption, $q_{max,exp}$, for the lowest initial concentration (C$_o$ = 2.00 $\times 10^{-5}$ mol L^{-1}) of 5.5´-DI were (4.11, 3.07 and 3.38) $\times 10^{-4}$ g g^{-1}; for C$_o$ = 2.99 $\times 10^{-5}$ mol L^{-1} (6.81, 5.48 and 4.18) $\times 10^{-4}$ g g^{-1} and for C$_o$ = 4.00 $\times 10^{-5}$ mol L^{-1} (5.29, 6.74 and 5.83) $\times 10^{-4}$ g g^{-1} at 283 K, 298 K and 313 K, 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, as a hypothetical model presented in the Fig. 5.
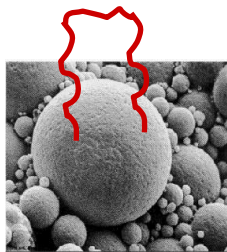
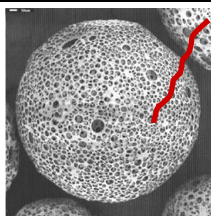**Figure5.** *A hypothetical representation of occupation of the active sites in pseudo-second order model*

In the lowest initial concentration (C$_o$ = 2.99 $\times 10^{-5}$ 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 (0.05 $\times 10^3$ min^{-1}), 298 K (0.09 $\times 10^3$ min^{-1}) and (0.21 $\times 10^3$ 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, $q_{max,calc}$, for C$_o$ = (2.00, 2.99 and 4.00) $\times 10^{-5}$ 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 [53-56].

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 [60] was also evaluated. The rate parameters for intraparticle diffusion (k_P) may be obtained by using eq. (7), where q_t is the amount of 5,5´-DI on peat at different times, t (min):

$$q_t = k_P t^{1/2} + B \tag{7}$$

k_P is the intraparticle diffusion rate constant (min$^{-1/2}$ g$_{5,5´-DI}$ / g$_{peat}$). According to eq.(7), 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. The intraparticle diffusion model could be applied to experimental data obtained in different initial concentrations for FP and DP (Table 7). 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 each peat. 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 [35]. A hypothetical representation of occupancy of sites in the intraparticle diffusion model is shown in Fig. 6.

Figure6. *A hypothetical representation of occupation of the active sites an intraparticle diffusion model.*

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$_{5,5´\text{-DI}}$ / g$_{peat}$) and the correlation coefficients for all 5,5´-DI initial concentrations investigated are shown in Table 7. 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 [45] and an irregular variation of the diffusion rate with initial 5,5´-DI concentration and temperature were observed.

Table7. *Intraparticle diffusion parameters for the adsorption of 5,5´-DI onto fibrous peat (FP) and decomposed peat (DP), C_o (initial concentration), k_P (min$^{-1/2}$ g $_{5,5´\text{-DI}}$ g^{-1} $_{FP}$).*

C_o (mol L^{-1})	T (K)	FIBROUS PEAT (FP)		DECOMPOSED PEAT (DP)	
		$k_P \times 10^5$	r^2	$k_P \times 10^5$	r^2
2.00×10^{-5}	283	3.02±0.02	0.9829	2.90±0.03	0.9683
	298	2.72±0.01	0.9982	1.97±0.02	0.9750
	313	2.53±0.01	0.9976	2.43±0.01	0.9824
2.99×10^{-5}	283	2.96±0.01	0.9909	2.67±0.01	0.9902
	298	4.18±0.02	0.9886	4.78±0.01	0.9965
	313	5.76±0.03	0.9863	5.75±0.03	0.9463
4.00×10^{-5}	283	3.01±0.01	0.9957	3.78±0.02	0.9704
	298	4.79±0.04	0.9475	4.92±0.05	0.9371
	313	5.48±0.01	0.9926	5.89±0.03	0.9526

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]. Fibrous peat (FP) and decomposed peat (DP) 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 peat, 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 (2.00, 2.99 and 4.00) $\times 10^{-5}$ mol L^{-1} the intraparticle diffusion constant increase too (Table 7).

4. CONCLUSIONS

Peat showed considerable potential low cost adsorbent for its use in the adsorption of 5,5´-DI from aqueous solution. The fibrous peat shows higher adsorption capacity than the decomposed peat, while under the same work conditions. 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 60 minutes for both temperatures and dye initial concentration. The pseudo-second order adsorption model adequately represents the interaction of 5,5´-DI with FP and DP, showing that adsorption occurs by the occupation of two active sites on the surface of the bio(adsorbent) as reported in literature [53-56]. Considering adsorption, desorption, kinetic modeling and physical properties of the adsorbent, peat is an appropriate material in future analytical applications.

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