

FULL PAPER

Evaluation of the Influence of Pre-treatment Temperature of *Leucaena leucocephala* in the Biosorption of 5G Blue Dye

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Abstract:

Leucaena leucocephala is an invasive exotic tree plant, and because of these characteristics, it becomes an environmental problem. In this sense, the main objective of the present study was to evaluate the adsorption capacity of 5G blue dye, using dry *L. leucocephala* leaves under different temperatures. Drying kinetic, centesimal composition and micrographs after drying of the leaves were also evaluated. For drying, the Valcan model best described the process kinetics, presenting a correlation coefficient of 99.4% and an average error of 1.41%. For the centesimal composition, 3.9% of moisture, 7.5% of ash, 23.8% of crude protein, 29.5% of crude fiber, 3.9% of etheral stratum and 31.4% of soluble carbohydrate were obtained. In the evaluation of the adsorptive capacity, the temperature of 40 °C was the one that produced the largest adsorbed amount of dye mass/leaf mass, 9.4 mg g⁻¹. The qualitative results obtained agreed with the one observed in the micrographs, so that the leaves of *L. leucocephala* have, therefore, industrial application with biosorbent.

Keywords: centesimal composition; drying kinetic; mathematical models; water pollution

1. Introduction

Leucaena leucocephala, Figure 1 (a) (b), is an arboreal/shrub species native of Central America that has spread to all tropical regions. Belonging to the Fabaceae family and of perennial behavior, this tree is used in the production of wood, charcoal, reforestation, green manuring and in animal nutrition and feeding [1]. Also, *L. leucocephala* is an alternative adsorbent that can be used in the treatment of textile effluents [2]. However, like all biomass adsorbents, leaves of *L. leucocephala* must be previously dried to be used in the treatment process of effluents [3].

The drying process is quite complex and involves the transfer of mass and heat between the drying air and the product to be dried, when as temperature rises, the partial vapor pressure in the product also increases, causing the reduction of the content of water and consequently the

reduction of metabolic, enzymatic, bacterial and fungal activities in the leaf [4,5].



Figure 1. (a) tree, (b) leaves and pods of *Leucaena leucocephala*.

It is found in the literature several mathematical models used in the representation of the kinetics of leaf drying, these evaluate external variables that act on the product during

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its water loss, among which we can mention the relative humidity of the air, the temperature and the speed of the air. The theoretical mathematical model considers only the internal resistance to heat transfer and water between the hot air and the product, and the empirical and semi-theoretical models consider only the external resistance to the relative humidity of the drying air and the temperature [6].

Leaves need to be dried after harvest to avoid deterioration and to standardize the raw material, thus facilitating the storage, transportation and use of the product. To the drying process to be effective and provide the desired characteristics for the leaf, it is necessary to know its thermophysical characteristics, since they are directly linked to mass and energy transfer [7]. Knowing the properties of the sheets is essential for determining the thermophysical properties of the material, since the variation of the components and their behavior during heat treatment influence the modeling, simulation and optimization of the process [8].

The textile industry is one of the main industrial sectors responsible for environmental pollution, since its effluents contain dyes and these, besides being highly toxic to living organisms, are extremely difficult to be degraded due to their essentially aromatic molecular structure. Therefore, there are several methods used in the

treatment of this type of effluent, we can mention the physical, chemical and biological [9,10].

Adsorption is a physical process which consists in the use of an adsorbent to retain and concentrate dyes on the surface. It is a technique that has been emphasizing, both from an environmental and economic point of view, its efficiency in the treatment of textile effluents, this is due to its ease of implementation and operation, besides having a relatively low cost depending on the material used as adsorbent [6]. Thus, the use of biological materials, available in abundance in nature, in the removal of dye-containing effluents is increasingly found in the literature.

In this sense, the main objective of the present study was to evaluate the adsorption capacity of 5G blue dye, using dry *L. leucocephala* leaves under different temperatures. Drying kinetic, centesimal composition and micrographs after drying of the leaves were also evaluated.

2. Results and Discussion

Drying Kinetics

Table 1 shows the values obtained by the statistical tests (DR, R^2 and SQR) performed for each empirical model adjusted to the experimental data of the drying kinetics of *L. leucocephala* leaves.

Table 1. Statistical evaluation of results.

Condition	Statistical Test	Henderson and Pabis [11]	Logarithmic [12]	Thompson [13]	Valcam [14]
40 °C	DR (%)	1.783	1.998	4.404	1.896
	R^2	0.981	0.982	0.993	0.999
	SQR	2.27×10^{-3}	2.18×10^{-3}	2.12×10^{-3}	2.15×10^{-3}
50 °C	DR (%)	6.451	1.435	11.67	1.274
	R^2	0.987	0.999	0.959	1.000
	SQR	2.30×10^{-4}	1.30×10^{-5}	7.38×10^{-4}	8.84×10^{-6}
60 °C	DR (%)	6.406	2.042	12.31	1.573
	R^2	0.974	0.986	0.959	0.986
	SQR	5.93×10^{-3}	5.58×10^{-3}	6.47×10^{-3}	5.59×10^{-3}
70 °C	DR (%)	10.21	1.46	18.11	0.912
	R^2	0.983	0.999	0.946	1.000
	SQR	4.11×10^{-4}	1.27×10^{-5}	1.27×10^{-3}	3.41×10^{-6}

It is possible to verify that all the models presented coefficient of determination (R^2)

superior to 0.95, being the model of Thompson an exception, when presenting a lower coefficient to

this one. Thus, for a more accurate analysis, it was necessary to use other statistical parameters, such as the sum of the squares of the residuals (SQR) and the relative deviation (DR).

From the analysis of the values obtained by the parameters SQR and DR, it is observed that, for the respective conditions under study, the model that presented the lowest values among all the models tested was Valcam, followed by the logarithmic model.

The Valcam model, proposed by Siqueira *et al.* (2013) [14], is an empirical model, in which the mass transfer of leucena leaves to warm air, represented by the humidity variation, which is directly influenced by the heat transfer from the air for the leaves, it is directly proportional to the drying time. This drying time, according to Valcam's model, is represented by a polynomial whose order is two.

Thus, to observe the good fit of the Valcam model, its drying curves are presented in Figure 2, where the continuous line represents the values calculated by the model and the discrete points represent the experimental data.

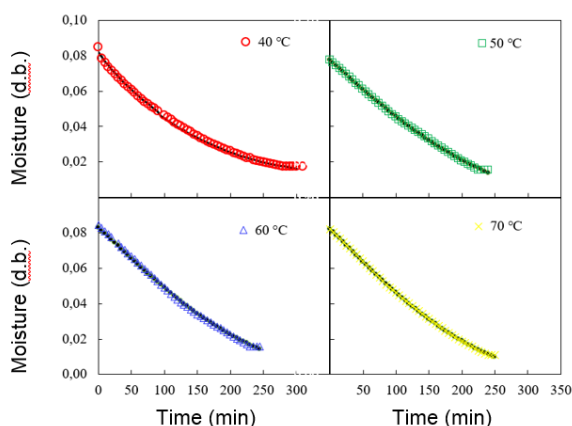


Figure 2. Kinetic drying of *L. leucocephala* leaves.

From Figure 2, as expected, as the temperature of the drying air has risen, the time required to reach the balance between the sheets and the drying air has decreased.

Evaluation of the centesimal composition

From the methodology described and from Equations (1) to (11), the percentages of moisture, ash, crude protein, crude fiber, lipid (etheral extract) and carbohydrate present in leaves of *L. leucocephala* in dry basis (Table 2).

Table 2. Percent composition of *L. leucocephala* leaf on dry basis.

Component	%
Moisture	3.89
Ash	7.47
Crude Protein	23.82
Crude Fiber	29.53
Lipid	3.93
Soluble Carbohydrate	31.36

According to the data presented in Table 2, the centesimal composition of the leaves of *L. leucocephala* presented, in ascending order of percentage, 31.36% of soluble carbohydrate, 29.53% of crude fiber, 23.82% of crude protein, 7.47% of ash, 3.93% lipid and 3.89% moisture.

In the literature, Zanu *et al.* (2012) obtained similar values for the centesimal composition of *L. leucocephala* leaves from the Ghana region: non-soluble carbohydrates 36.01%, crude fiber 14.30%, crude protein 23.44%, ashes 11.20% lipid 6.40% and humidity 8.65% [15]. In the literature, the composition obtained by Kasiga *et al.*, (2014), also presented approximate values to those obtained in the present study: 40% soluble carbohydrate, 14% crude fiber, 25% crude protein, 5% ash and 8% lipid [16].

The results obtained compared to the literature show that there is a pattern in the composition of the leaves.

According to Van Soest (1994), the composition of the plants is directly related to the soil and climate of the environment in which they develop. Plants use solar radiation, ambient humidity and soil nutrients in their development and maintenance, therefore external factors such as climate and soil directly interfere with leaf composition [17].

The physicochemical nature of the adsorbent is a determining factor as the capacity and rate of adsorption depend on the functional groups present on the surface of the adsorbent and the nature of the precursor material. Thus, the evaluated components may give indications of the

most abundant compounds in the material that will directly influence the adsorption process [18].

Evaluation of Micrographs

The micrographs, shown in Figure 3 (a), (b) and (c), show the formation of smaller cracks and less destruction of the pores in the dry leaves at 40 °C than the dry leaves at 70 °C, this shows that possibly leaves treated at lower temperatures will have smaller cracks and more likely to adsorb the dye.

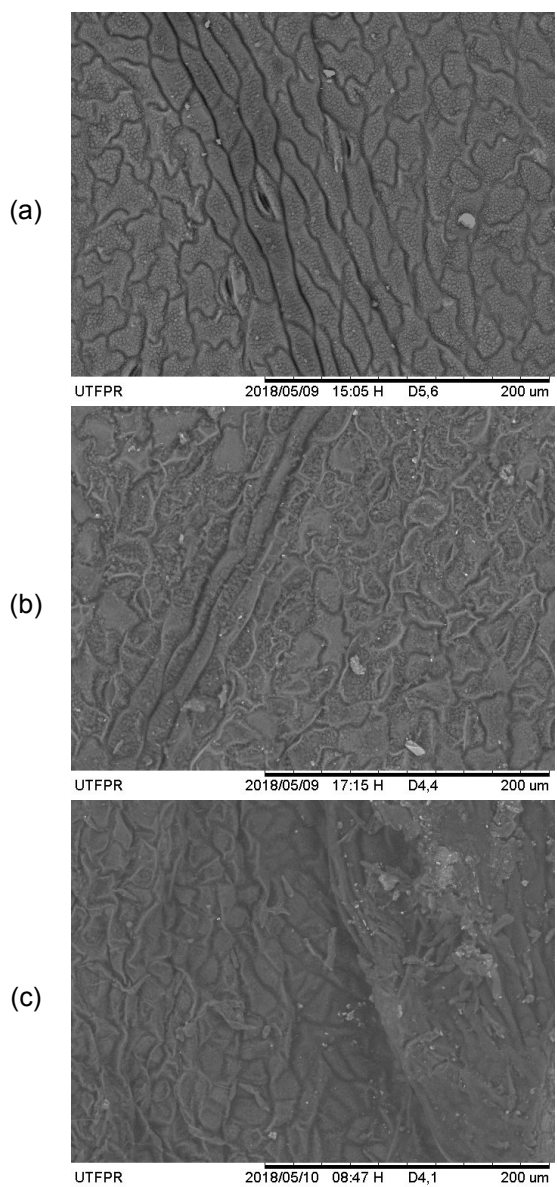


Figure 3. (a) Fresh leaf (b) Dried leaf at 40 °C (c) Dried leaf at 70 °C.

Evaluation of the drying temperature in the dye removal Reactive Blue 5G

The influence of the drying temperature of the *L. leucocephala* leaves on the ability to remove the reactive blue dye 5G can be observed according to Figure 4. From this, the lower temperature (40 °C) was highlighted among the others in analysis, being able to remove a greater amount of dye, about 7.60 mg g⁻¹.

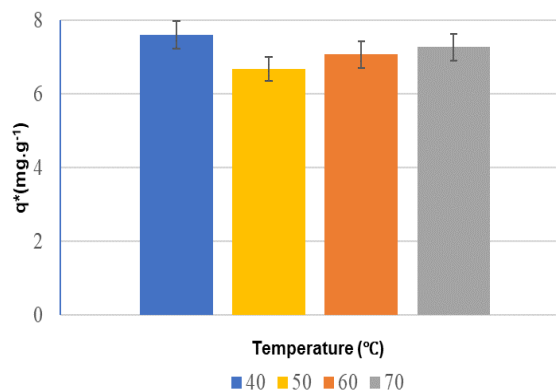


Figure 4. Influence of the drying temperature of the leaves of *L. leucocephala* on the adsorption capacity of the dye Blue Reactive 5G in solution of pH 2 and solution temperature of 30 °C.

For statistical evaluation of the influence of each of the drying temperatures evaluated in the dye removal, a Variance Analysis (ANOVA) was performed based on the values obtained experimentally. Table 3 demonstrates this analysis.

Table 3. Analysis of variance, with a significance level of 95%, of the influence of the drying temperature of the biosorbent in the removal of the reactive blue dye 5G.

	SQ	GL	MQ	F	p
Treatment	1,35587	3	0,451955	1,326	0,3319
Residue	2,7257	8	0,340713		

In this way, a p-value greater than 0.05 was obtained through this analysis, and the hypothesis that the tested groups do not influence the amount of adsorbed dye is not rejected, that is, the different temperatures do not alter the dye retention capacity.

Thus, despite having proved statistically that the different drying temperatures of the biosorbent do not influence the adsorption process of the

reactive blue dye 5G, to reduce energy costs and a better process efficiency, the lower drying temperature should be made.

3. Material and Methods

The *L. leucocephala* leaves were collected on the morning of April 29, 2017, in the city of Dois Vizinhos-PR. The pines were plucked and stripped manually, as shown in Figure 5. The collected material was packed into plastic discs and kept under refrigeration to ensure that all the pastes were removed from the same matrix.



Figure 5. Leaves of *L. leucocephala* after harvest.

Drying Kinetics

The thin layer samples were dried in a forced circulation oven, and the temporal variation of humidity was monitored at 5-minute intervals. An analytical balance was used to determine the mass. The samples were dried to constant mass in two consecutive weighing. The experiments were conducted at temperatures of 40, 50, 60 and 70 °C, and their respective influences on drying kinetics were studied. The dry matrix mass was determined after drying in an oven for 24 hours at 105 °C. All experiments were conducted in triplicate. The parameter adjustments of the simplified drying kinetics models listed in Table 4 were tested.

In what is the moisture in dry basis (d.b.), k , a , b , c and d are constants of the models, and t is the drying time (min).

In the adjustment of the parameters of the empirical models to the experimental data, Statistica software was used. The parametric optimization method employed was Levenberg-Marquardt, with convergence criterion 10⁻⁶. To

verify the adequacy of the results obtained by the models to the experimental data, the statistical tests of relative deviation, DR, coefficient of determination, R², and sum of the square of the residuals, SQR.

Table 4. Empirical models of drying kinetics.

Model	Mathematical Expression
Henderson and Pabis [11]	$X = a \exp(-kt)$
Logarithmic [12]	$X = a \exp(-kt) + c$
Thompson [13]	$X = \exp(-a \frac{(a^2 + 4bt)^{0.5}}{2b})$
Valcam [14]	$X = a + bt + ct^{1.5} + dt^2$

Centesimal Composition

To obtain the bromatological composition, dry matter, mineral matter, crude protein, neutral detergent fiber, acid detergent fiber, ethereal extract and soluble carbohydrate were evaluated in triplicates. All analyzes were carried out in the premises of the Bromatology, Ecology and Bioprocess Engineering and Biotechnology Laboratories, of Federal Technological University of Paraná Campus Dois Vizinhos.

After pre-drying, the *L. leucocephala* leaves were weighed and ground in a knife mill. Dry matter and ash, or mineral matter, were obtained by the AOAC technique (1998) [19]. For the determination of the crude protein, the Kjeldahl method [20] was used. The neutral detergent fiber and acid detergent fiber was determined by the technique of Van Soest (1963) [21]. The analysis of ethereal extract was performed with the aid of an Ankon equipment, ANKOM XT15 Extractor, which adapts the technique described by AOAC (1998) [19]. The soluble carbohydrate was determined by difference in relation to the other components [22].

Micrographs

The micrographs of the leaves *in natura*, dried at 40 and 70 °C were carried out at the analytical plant of the Federal Technological University of Paraná Campus Pato Branco, with Hitachi 3000 equipment.

Adsorption capacity of 5G blue dye

Approximately 0.2 g of dried leaves of *L. leucocephala* were weighed at different temperatures and 50 ml of 0.05 g L⁻¹ dye solution was added with an experimental pH of 2, adjusted with hydrochloric acid in an erlenmeyer, which were subjected to constant agitation of 150 rpm and temperature of 30 °C for 48 hours in SOLAB equipment, refrigerated SHAKER incubator SL-223.

After the procedure, the contents of the erlenmeyers were centrifuged and the absorbances were measured in the GENESYS 10S UV-Vis spectrophotometer at 623 nm. By means of a linear calibration curve that relates absorbance and concentration, this was identified for each of the adsorption tests developed in this work. The removal capacity was calculated by Equation 12.

$$q = \frac{V \times (C_0 - C)}{m} \quad (12)$$

Where C_0 and C are initial and equilibrium concentrations of the dye in the liquid phase, respectively (mg L⁻¹), V is the volume of solution (L) and m is the mass of solid (g).

4. Conclusions

Statistical tests on drying kinetics showed that the Valcam model best approximate the behavior of the leaf during drying, followed by the logarithmic model. As expected, the lower the temperature the higher the residence time in the drying process should be until the mass balance is reached.

The analysis of the composition showed that in one gram of leaf, dry basis, it consists of 0.314 g of soluble carbohydrate, 0.295 g of crude fiber, 0.238 g of crude protein, 0.075 g of mineral matter, 0.0393 g of ethereal stratum and 0.039 g of water. The results obtained were consistent with those found in the literature and will serve as a basis for calculations of thermophysical properties in the future.

The micrographs show that at 40 °C there is the formation of cracks and pores without destruction of the structure of the sheet, already

to 70 °C, the drying process appears to destroy the pores and cracks in the process of water removal.

The statistical tests show that there was no difference in the pretreatment of the leaves for the dye adsorption process, so it is defined that the best temperature for treatment of the biosorbent is 40 °C, considering the energy expenditure for this drying. Further tests should be performed to evaluate the best conditions of use of leucine in the reactive 5G dye adsorption process.

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