

## Tannery wastes-derived gelatin and carbon nanotubes composite beads: adsorption and reuse studies using tartrazine yellow dye

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### ABSTRACT

Tartrazine yellow is a dye commonly used in the food, textile, cosmetic and pharmaceutical industries. The effluents generated containing this contaminant must be treated since it presents potential carcinogenicity to the cells. The adsorption stands out among the other techniques used to remove dye from wastewater due to its ease of operation and implementation, and high removal rate. However, the production of effective and low-cost adsorbents is a constant challenge. Gelatin is a promising compound for the production of adsorbent composites, enabling the improvement of its low mechanical properties and accelerated degradation, by the addition of carbonaceous, such as carbon nanotubes (CNT's). Taking into account economic and environmental aspects, gelatin can be recovered from chromium-tanned leather wastes (RCTLW). Thus, this work aimed to study the adsorption of the tartrazine yellow dye by adsorbent composites based on: (1) commercial gelatin/CNT's beads and (2) RCTLW gelatin/CNT's beads. Commercial and RCTLW gelatin composite beads showed an adsorption capacity of 202.39 and 131.32 mg.g<sup>-1</sup>, respectively, estimated by the Langmuir model. In adsorption kinetics, the density continued to increase after 300 min for both the composite materials, with better prediction of the pseudo-first order model. In the reuse study, the commercial and RCTLW gelatin composite beads proved to be usable for up to 10 cycles, with regenerations of 45 to 68% and 45 to 61%, respectively. In general, the composite beads of gelatin showed promise for the adsorption of dyes, mainly RCTLW gelatin, since it makes possible the use and minimization of wastes.

**Keywords:** leather waste; biopolymer; removal; tartrazine.

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### 1 INTRODUCTION

Synthetic dyes are widely used by industries to improve the consumption characteristics and appearance of their products. However, during processing, the dyes don't completely fix in the manufactured products, generating colored effluents [1-4].

In the food, textile, cosmetic and pharmaceutical industries, the Tartrazine yellow dye (TYD) is commonly used. Regarding its molecular structure, it has aromatic rings and its metabolic and degradation products (aromatic amines, benzidines and benzene sulfonic acids) are carcinogenic, mutagenic and DNA adducts, and can induce harmful effects to cells [5, 6].

The techniques commonly used for the treatment of wastewater to remove dyes are flocculation/coagulation, precipitation, photocatalytic degradation, biological oxidation, ion exchange, advanced oxidative processes, bioremediation, membrane separation, and adsorption [7, 8]. The adsorption stands out due to its ease of operation and implementation, high removal rate, and low cost, depending on the adsorbent material used [9]. In this context, obtaining and producing effective and low-cost adsorbents are constant challenges because, in addition to the economic bias and adsorption capacity, the material must show chemical, mechanical stability, and potential for reuse [10].

Gelatin is a promising adsorbent material, as it presents favorable characteristics such as biodegradability, low cost, wide availability, capacity to form a gel, and to have a chemical structure and surface that is favorable to adsorption [11-13]. However, as a disadvantage, gelatin when in its natural form has low mechanical resistance and accelerated degradability in wet conditions, factors that limit its application as an adsorbent [14].

Therefore, the production of composite materials has been widespread in the adsorption area, aiming to improve the mechanical, thermal, and chemical properties of the base adsorbent material, uniting it with other compounds [15]. One of the materials that can be used to obtain composite materials are carbon nanotubes (CNT's), which have high hydrothermal stability, high surface/volume ratio, and excellent mechanical properties, thus overcoming the disadvantages of gelatin as an adsorbent [16-19].

Also, gelatin can be recovered from chromium-tanned leather waste (RCTLW), adding value to an industrial waste generated in several countries, with high polluting potential, minimizing environmental impacts [20-23]. It is also noteworthy that, several studies have addressed the use of commercial gelatin as a basis for the production of adsorbent composites for the removal of dyes [24], metals [25], and drugs [26], however, research using gelatin recovered from residual sources for use as an adsorbent is scarce.

Thus, this work aimed to study the adsorption of the tartrazine yellow dye by an adsorbent composite from gelatin recovered from chromium-tanned leather wastes (RCTLW) and carbon nanotubes (CNT's). For comparison purposes, commercial gelatin/CNT's beads were also used in the adsorption tests.

## 2 MATERIALS AND METHODS

### 2.1 Materials

The materials used in this work were commercial gelatin powder type B (La Casella, Brazil), multi-walled carbon nanotubes functionalized by oxidation (Nanotec, UFMG, Brazil) with a surface area of  $132.99 \text{ m}^2 \cdot \text{g}^{-1}$  and pore radius of  $18.29 \text{ \AA}$ , glutaraldehyde (Neon, Brazil), acetone (Neon, Brazil), and tartrazine yellow dye (Duas Rodas, Brazil). All reagents used were of analytical grade.

The chromium-tanned leather wastes were kindly donated by a leather company in the north of the state of Rio Grande do Sul, Brazil.

### 2.2 Extraction and concentration of gelatin from tannery wastes

The extraction of gelatin RCTLW was performed by alkaline hydrolysis according to the method of SCOPEL *et al.* [23]. The concentration was carried out in membranes, followed by precipitation in ice-cold acetone at  $-4 \text{ }^\circ\text{C}$ , according to the method described by RIGUETO *et al.* [20].

### 2.3 Synthesis and characterization of composite beads

The composite beads were prepared by the drip emulsification method described by RIGUETO *et al.* [20] adapted from SABER-SAMANDARI *et al.* [16].

The characterization of composite beads has been previously reported by RIGUETO *et al.* [20], and shows diameters less than 1.5 mm, point of zero charge around 5.0, capacity to swell twice as much as its own size, and water retention capacities close to 80%.

Figure 1 summarizes the synthesis of the beads and the characterization already reported.

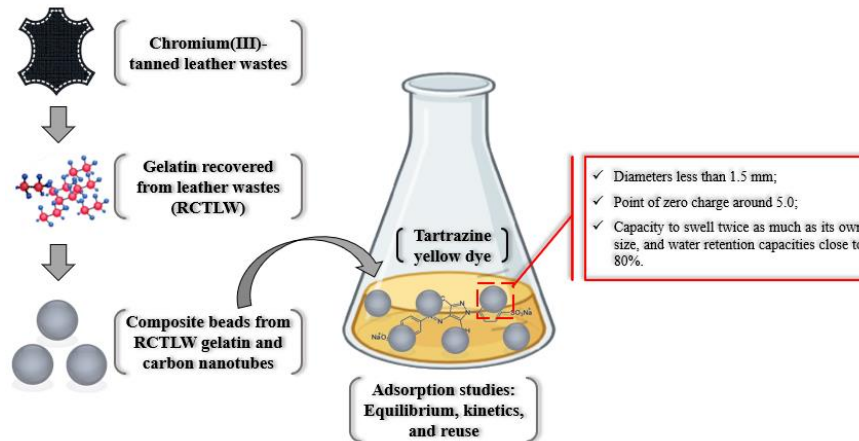


Figure 1: Graphical abstract of the synthesis and characterization steps of gelatin-based composite beads

### 2.4 Batch adsorption tests

The equilibrium and adsorption kinetics tests were performed by the batch system, and the pH of the solutions of TYD was adjusted to 2.5, as suggested by DOTTO *et al.* [27]. Adjustments were made using 0.05 mol.L<sup>-1</sup> HCl or NaOH solutions.

Initially, equilibrium tests were performed to construct the adsorption isotherms, using an adsorbent dosage of 0.4 g.L<sup>-1</sup> of the composite beads and 50 mL of the TYD solution in concentrations of 37.5, 50, 100, 150, 200, 300, and 400 mg.L<sup>-1</sup>, in 250 mL conical flasks, maintained at 25 °C, and 120 rpm in a shaker incubator (Marconi, MA-420, Brazil). The absorbance readings were performed at 1h intervals until the adsorption equilibrium was established.

The adsorption kinetics was performed using 50 mL of the TYD solution, in the initial concentration of 100 mg.L<sup>-1</sup> and adsorbent dosage of 0.4 g.L<sup>-1</sup>, in 250 mL conical flasks, maintained at 25 °C and 120 rpm in a shaker incubator (Marconi, MA-420, Brazil). Readings were taken at 10, 15, 30, 45, 60, 90, 120, 150, 180, and 210 min.

All tests were performed in duplicate, with subsequent reading on a spectrophotometer (Tecnal, UV-5100, Brazil), at a wavelength of 429 nm and an external calibration curve was used to quantify the tartrazine yellow dye. From the concentration data obtained, the amount of adsorbed was calculated according to Equation 1.

$$q = \frac{V(C_0 - C)}{m} \tag{1}$$

Where, q the amount of dye adsorbed per gram of water bath root (mg g<sup>-1</sup>), C<sub>0</sub> and C dye concentration in the initial and final aqueous solution respectively (mg L<sup>-1</sup>), V the volume of dye solution (L), and m the mass of biosorbent (g).

The equilibrium was defined when the concentration of the dye showed standard error between its measurements of less than 5% in 3 measurements at 1h intervals.

### 2.5 Mathematical modeling

In mathematical modeling, the Langmuir, Freundlich, and Redlich-Peterson models were fitted to the experimental equilibrium data, while the pseudo-first order, pseudo-second order, and Elovich models to the kinetic experimental data, as shown in Table 1.

Table 1: Kinetic and equilibrium models used in mathematical modeling of experimental adsorption data of TYD by gelatin composite beads

MODEL	EQUATIONS
<b>KINETIC MODELS</b>	
Pseudo-first order	$q(t) = q_1(1 - e^{-k_1t})$ (2)

Pseudo-second order	$q(t) = \frac{t}{(1/k_2q_2^2) + (t/q_2)}$	(3)
Elovich	$q(t) = \frac{1}{\beta} \ln(1 + \alpha\beta t)$	(4)
<b>ISOTHERM MODELS</b>		
Langmuir	$q_e = \frac{q_m K_L C_{eq}}{1 + K_L C_{eq}}$	(5)
Freundlich	$q_e = K_F C_e^{1/n_F}$	(6)
Redlich-Peterson	$q_e = \frac{K_{RP} C_e}{1 + \alpha C_e^\beta}$	(7)

Where:  $k_1$  ( $\text{min}^{-1}$ ) rate constant of pseudo-first-order,  $q_1$  ( $\text{mg.g}^{-1}$ ) theoretical value of adsorption capacity,  $k_2$  ( $\text{g.mg}^{-1}.\text{min}^{-1}$ ) rate constant of pseudo-second-order,  $q_2$  ( $\text{mg.g}^{-1}$ ) theoretical value of adsorption capacity,  $\alpha$  ( $\text{mg.g}^{-1}.\text{min}^{-1}$ ) initial rate of adsorption and  $\beta$  ( $\text{g.mg}^{-1}$ ) is the desorption constant of Elovich model,  $q_m$  ( $\text{mg.g}^{-1}$ ) maximum adsorption capacity,  $K_L$  ( $\text{L.mg}^{-1}$ ) Langmuir constant,  $K_F$  ( $\text{mg.g}^{-1}$ ) ( $\text{mg.L}^{-1}$ )<sup>-1/n</sup> Freundlich constant,  $1/n$  (-) heterogeneity factor,  $K_R$  ( $\text{L.g}^{-1}$ ) Redlich-Peterson constant;  $\alpha$  ( $\text{mg.L}^{-1}$ )<sup>- $\beta$</sup>  Redlich-Peterson constant,  $\beta$  (-) heterogeneity factor.

The models presented in Table 1 were fitted to the experimental data by the nonlinear regression technique, through the Gaus-Newton method, by minimizing the objective function sum of squares of the residues. The modeling mathematical was performed using the software Statistica 7.0 (Statsoft, USA).

## 2.6 Desorption and reuse studies

The desorption and reuse of composite beads were evaluated using the tartrazine yellow dye adsorption. In 50 mL Falcon conical centrifuge tubes, approximately 0.05 g of adsorbent and 30 mL of the 200  $\text{mg.L}^{-1}$  TYD solution were added, with a pH previously adjusted to 2.5. The tubes remained in the shaker at 120 rpm and 25 °C for 2h. Subsequently, an aliquot of the solutions was collected for spectrophotometric reading, and the removal capacity was calculated according to Equation 8.

$$\text{Removal (\%)} = \left( \frac{C_0 - C_{ads}}{C_0} \right) \times 100 \quad (8)$$

where  $C_0$  is the initial concentration ( $\text{mg.L}^{-1}$ ) and  $C_{ads}$  is the final concentration after the adsorption cycle ( $\text{mg.L}^{-1}$ )

For the desorption tests, after the mentioned adsorption step, the composite beads were washed with distilled water to remove the dye solution present on the surface, and then, in 50 mL Falcon conical centrifuge tubes, 0.05  $\text{mol.L}^{-1}$  NaOH solution was added remaining in a shaker (120 rpm, 25 °C) for 15 min. Afterward, aliquots of the samples were taken to read the concentration in a spectrophotometer, and then, the degree of regeneration was calculated, according to Equation 9.

$$\text{Regeneration (\%)} = \frac{(m_{des} \times 100)}{m_{ads}} \quad (9)$$

where  $m_{des}$  is the amount of dye adsorbed in the desorption cycle (mg), and  $m_{ads}$  is the amount of dye adsorbed in the adsorption cycle (mg).

Ten adsorption/desorption cycles were evaluated and the percentage of removal and regeneration was determined in each cycle.

### 3 RESULTS AND DISCUSSION

#### 3.1 Adsorption isotherms

To evaluate the adsorption, it is necessary to produce equilibrium curves by means of adsorption isotherms at equilibrium. These curves are projected through a relationship between equilibrium adsorption capacity ( $q_e$ ) versus equilibrium adsorbate concentration in the fluid phase ( $C_e$ ), at a constant temperature [28]. These curves demonstrate an adsorption capacity of an adsorbent by a solute under the adopted experimental conditions [29].

The adsorption isotherms of the TYD by the commercial/CTN's beads and RCTLW gelatin/ CNT'S beads are shown in Figure 2 (a) and (b), respectively.

The profiles of equilibrium curves (Figure 2), can be classified according to GILES *et al.* [30], for TYD adsorption, the isothermal curves have an "H1" and "L2" profile for Commercial and RCTLW gelatin composite beads, respectively. Class L curves (Normal or Langmuir type) describes that as adsorption occurs, fewer active sites will be available and there will be less probability that a solute molecule will bind to the adsorbent, so to increase the solute adsorption, higher concentrations of the solution are needed. Class H curves (high affinity) shows that there is a high affinity between adsorbate and the adsorbent, indicating chemical adsorption and by electrostatic forces. Also, Subclass 1 for class H shows that the adsorption sites were not fully occupied and suggests a Freundlich isotherm. Subclass 2 for class L and H describes that there was complete saturation of the adsorbent monolayer, where the solute has a high affinity for the solvent, in this case, the data can be represented by Langmuir isotherm [30, 31].

The adsorption isotherms models are used to understand the equilibrium relationship between the solid and liquid phases. These models have parameters that allow obtaining the maximum adsorption capacity, which indicates the quality of the adsorbent and also identifies the type of interaction between the adsorbent and adsorbate [31].

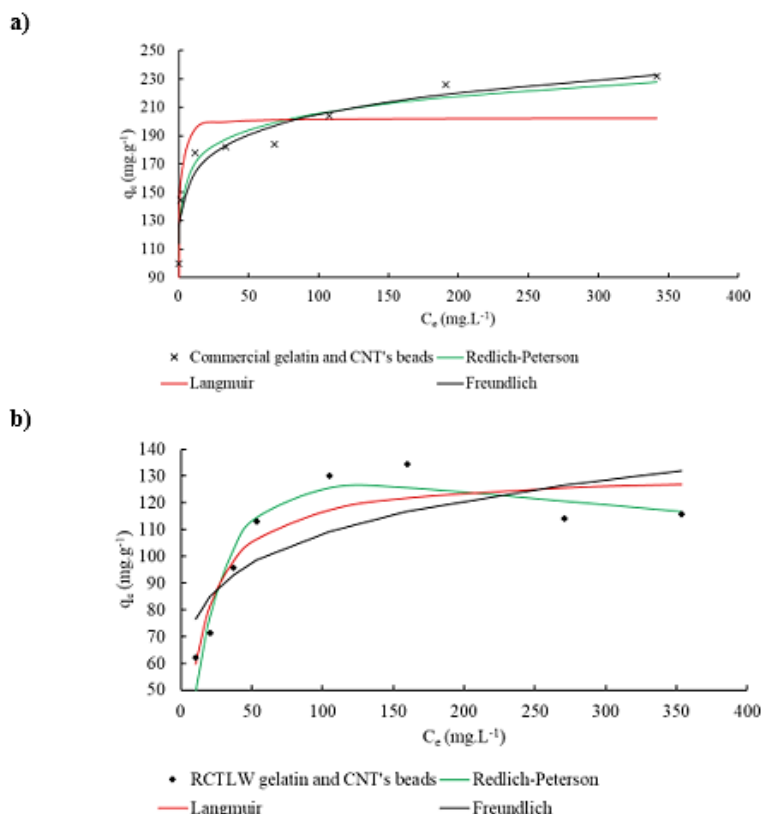
Table 2 presents the values of the parameters of the Langmuir, Freundlich, and Redlich-Peterson isothermal models fitted to the experimental data of adsorption of the TYD by the commercial gelatin/CNT's beads and RCTLW gelatin/CNT's beads.

Table 2 shows that the Redlich-Peterson model presented better fit to the experimental data, with coefficients of determination ( $R^2$  and  $R^2_{adj.}$ ) greater than or close to 0.9. Redlich-Peterson model combines elements of the Langmuir and Freundlich models, so that in low concentrations it follows the Langmuir model and in high concentrations it follows Freundlich model [32]. However, when the value of  $\beta$  is close to 1, the parameters  $q_m$  and  $KR$  are reduced to the parameters  $q_m$  and  $K_L$  of Langmuir [32]. Another interpretation that can be adopted is that the R-P model indicates a Freundlich isotherm when the constants  $KR$  and  $a_R \gg 1$  and  $\beta = 1$  [33].

According to the R-P parameters, commercial gelatin and CNT's beads present a  $\beta$  value close to 1, and values of  $K_R$  and  $a_R \gg 1$ , showing that the model that represents these data is the Freundlich model. For RCTLW gelatin/CNT's beads, the R-P model shows values of  $\beta$  close to 1, and values of  $K_R$  and  $a_R$  lower or tending to 1, then the model that represents these data is the Langmuir model.

Langmuir model presented better fits to RCTLW gelatin/CNT's beads data, indicating that adsorption doesn't occur beyond the monolayer coverage, the active sites are energetically homogeneous and each site can hold only one adsorbate molecule [31]. The maximum adsorption capacity (Table 2) for this material was  $131.32 \text{ mg.g}^{-1}$ .

Comparing the adsorption capacities of the tartrazine yellow dye, with the study by RIGUETO *et al.* [34] who used beads from commercial ( $257.46 \text{ mg.g}^{-1}$ ) and RCTLW ( $263.13 \text{ mg.g}^{-1}$ ) gelatins, without the addition of carbon nanotubes, it appears that the addition of this component to the matrix of the gelatin caused a reduction in the capacity and affinity adsorptions of the dye. This behavior may be associated with the point of zero charge of the CNT's, which is 3.10 (Annex A), this value being close to the pH of the dye solutions (2.5) used in the adsorption tests.



**Figure 2:** Adsorption isotherms of TYD (25 °C, 120 rpm, pH 2.5, and adsorbent dosage of 0.4 g.L<sup>-1</sup>) by (a) Commercial gelatin/CNT's beads and (b) RCTLW gelatin/CNT's beads

**Table 2:** Equilibrium model parameters for TYD adsorption by commercial gelatin/CNT's beads and RCTLW gelatin/CNT's beads

Isotherm/Parameter	Tartrazine yellow dye	
	Commercial gelatin/CNT's beads	RCTLW gelatin/CNT's beads
<b>Langmuir</b>		
$q_m$ (mg.g <sup>-1</sup> )	202.39	131.32
$K_L$ (L.mg <sup>-1</sup> )	2.17	0.08
$R^2$	0.78	0.83
$R^2_{adj}$	0.77	0.82
<b>Freundlich</b>		
$K_F$ (mg.g <sup>-1</sup> ) (mg.L <sup>-1</sup> ) <sup>-1/n</sup>	126.93	53.29
$n_F$ (-)	9.61	6.47
$R^2$	0.94	0.62
$R^2_{adj}$	0.93	0.60
<b>Redlich-Peterson</b>		
$K_R$ (L.mg <sup>-1</sup> )	1437.56	5.81
$a_R$ ((mg.L <sup>-1</sup> ) <sup>-β</sup> )	10.21	0.014
$β$ (-)	0.917	1.20
$R^2$	0.96	0.90
$R^2_{adj}$	0.95	0.89

Other studies that used gelatin-based composites for dye adsorption, reported the monolayer adsorption capacities estimated by the Langmuir model. ALINEJAD-MIR *et al.* [35] in the adsorption of direct yellow 12 from aqueous solutions using an iron oxide-gelatin nano adsorbent, found  $q_m=1250$  mg.g<sup>-1</sup> and SÄBER-SAMANDARI *et al.* [16] using gelatin-based magnetic nanocomposite beads comprising carboxylic acid functionalized carbon nanotube in the adsorption of methylene blue and direct red 80, obtained value of  $q_m=1428.5$  and 714.2 mg.g<sup>-1</sup>, respectively.

For commercial gelatin and CNT's beads, Freundlich model suggests that adsorption occurs on a heterogeneous surface, with energy and affinity non-uniform on the surface [36]. The parameter  $n_F$  also sug-

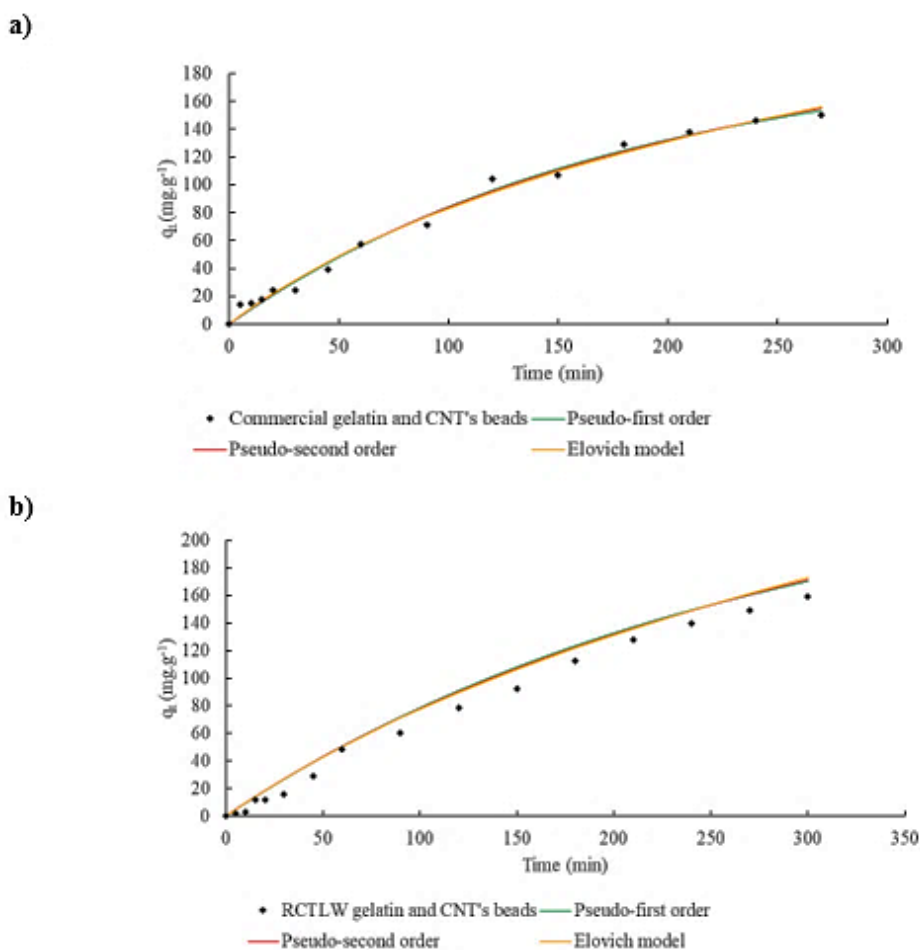
gests that adsorption is favorable when their values are between 1 to 10, in this work was obtained values of 9.61 and 6.47 (Table 2) for commercial gelatin/CNT's beads and RCTLW gelatin/CNT's beads, respectively.

Regarding to the dye adsorption mechanism by the gelatin composite beads, research reports that the main interaction is by electrostatic forces, and when in acid pH the amino and hydroxyl groups of gelatin are protonation, attracting the sulfonated groups of the dye structure favoring adsorption [37-39].

### 3.2 Adsorption kinetic

Adsorption kinetic is expressed as the mass transfer rate of compounds contained in the fluid phase to the adsorbent, and from it, the parameters obtained by modeling can be compared to the behavior of the adsorbent obtained experimentally [40, 41].

The kinetic data of the TYD adsorption (25 °C, 120 rpm, pH 2.5, and adsorbent dosage of 0.4 g.L<sup>-1</sup>) by the commercial gelatin/CNT's beads and RCTLW gelatin/CNT's beads are shown in Figure 3 (a) and (b), respectively.



**Figure 3:** Kinetic adsorption of TYD (25 °C, 120 rpm, pH 2.5, and adsorbent dosage of 0.4 g.L<sup>-1</sup>) by (a) Commercial gelatin/CNT's beads and (b) RCTLW gelatin/CNT's beads

In the adsorption of TYD (Figure 3) for both materials containing gelatin and CNT's, it's noted that the adsorption density continues to increase after 300 min, due to incomplete saturation of the adsorbent active sites by the dye.

Table 3 shows the values of the parameters of the kinetic models of Pseudo-first order, Pseudo-second order, and Elovich fitted to the experimental kinetic data of adsorption of TYD by commercial gelatin/CNT's beads and RCTLW gelatin/CNT's beads.

Table 3 shows that the PFO, PSO, and Elovich models had good coefficients of determination ( $R^2$  and  $R^2_{adj.}$ ) to the kinetic experimental. These good fits can be illustrated by means of graphics (Figure 3), in which the curves of the models overlap with the curve of the experimental data, showing a good fit of the models to the kinetic data.



**Table 3:** Kinetic model parameters for adsorption of TYD by commercial gelatin/CNT's beads and RCTLW gelatin/CNT's beads

Kinetic model/Parameter	Tartrazine yellow dye	
	Commercial gelatin/CNT's beads	RCTLW gelatin/CNT's beads
<b>Pseudo-first order</b>		
$q_1$ (mg.g <sup>-1</sup> )	197.9	254.8
$k_1$ (min <sup>-1</sup> )	0.0056	0.0037
R <sup>2</sup>	0.99	0.99
R <sup>2</sup> adj.	0.99	0.99
<b>Pseudo-second order</b>		
$q_2$ (mg.g <sup>-1</sup> )	309.66	428.84
$k_2$ (min <sup>-1</sup> )	1.2x10 <sup>-6</sup>	5.19x10 <sup>-6</sup>
R <sup>2</sup>	0.99	0.99
R <sup>2</sup> adj.	0.99	0.99
<b>Elovich</b>		
$\alpha$ (mg.g <sup>-1</sup> .min <sup>-1</sup> )	1.21	0.97
$\beta$ (g.mg <sup>-1</sup> )	0.0085	0.0055
R <sup>2</sup>	0.990	0.987
R <sup>2</sup> adj.	0.989	0.986
<b>qe experimentals (mg.g<sup>-1</sup>)</b>	183.90 <sup>a</sup>	110.10 <sup>b</sup>

<sup>a</sup> qe experimental calculated from the parameters of the Langmuir isotherm; <sup>b</sup> qe experimental calculated from the parameters of the Freundlich isotherm;

The experimental qe were calculated taking into account the best isotherm model that fit each type of material. In this case, the Freundlich model was used for commercial gelatin/CNT's beads and the Langmuir model for RCTLW gelatin/CNT's beads. Thus, it was found that the kinetic parameters in the adsorption of TYD, the values of qt experimental of the PFO model are closer to the experimental qe calculated by Freundlich and Langmuir models, respectively. Also, it notorious the PFO model overestimated the qt for RCTLW/CNT's beads. On the other hand, the PSO model overestimated the capabilities of adsorption for both materials.

The Elovich model also shows a determination coefficient close to 0.99 for both materials, and this model involves chemisorption in the solid surface, suggesting that the adsorption of the dye onto commercial and RCTLW gelatin/CNT's beads occurred by internal and external mass transfer [42].

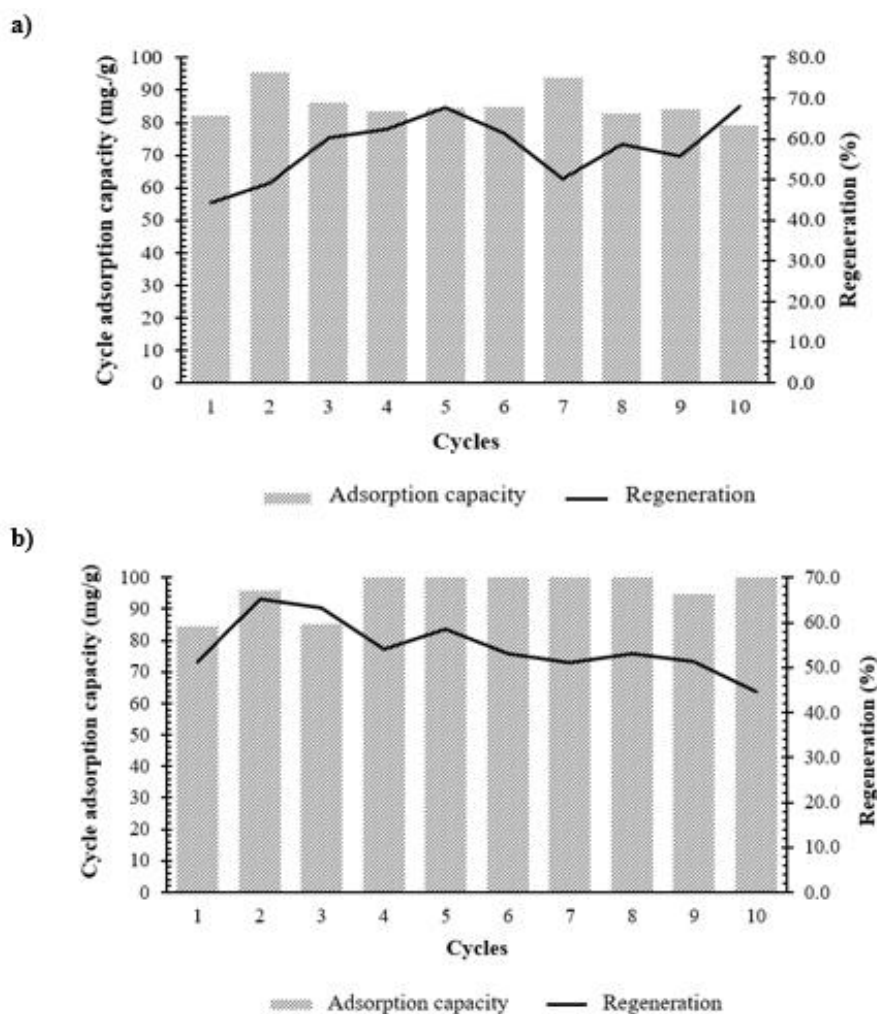
### 3.3 Desorption and reuse studies

Regeneration is used to remove the adsorbed accumulated on the surface of the material and thus recover the capacity of the absorbent. Regeneration increases the life cycle of the material, which means that less solids wastes are produced at the end of each process, making it possible a reduction in the economic and environment impact of the process [43].

Figure 4 (a) and (b) show the results of the desorption and reuse tests of the commercial and RCTLW gelatin and CNT's beads, in the adsorption of TYD.

Commercial gelatin/CNT's beads (Figure 4a), showed an adsorption capacity in the first cycle of 82 mg.g<sup>-1</sup>, varying between 80 to 95 mg.g<sup>-1</sup> from the second to the tenth cycle. The regeneration started at 45%, and varied from the second to the tenth cycle, in a range of 45 to 68%, ended with 68% of dye regeneration. For RCTLW gelatin/CNT's beads (Figure 4b) presented an initial adsorption capacity of 85 mg.g<sup>-1</sup>, with variations from 86 to 100 mg.g<sup>-1</sup>, from the second to the tenth cycle. The regeneration started with 51% varying between 45 to 65% over the cycles, ending the tenth and last cycle with 45% of dye regeneration.





**Figure 4:** Desorption and reuse tests (25 °C, 120 rpm, pH 2.5, and adsorbent dosage of 1.66 g.L<sup>-1</sup>) using (a) Commercial gelatin/CNT's beads and (b) RCTLW gelatin/CNT's beads

The use of NaOH 0.05 mol.L<sup>-1</sup> as an eluent for the desorption of TYD using commercial and RCTLW gelatin with CNT's beads, doesn't cause the reduction in the adsorption capacity of the composite, being possible to be used for 10 cycles. The NaOH in an aqueous solution makes the gelatin amine groups be deprotonated, causing the electrostatic interactions with the dye to break down.

Other researches evaluated the life cycle using gelatin-based adsorbent composites, for example, CHEN *et al.* [44] used gelatin/ $\beta$ -cyclodextrin composite fiber adsorbent for the adsorption of methylene blue, obtaining an adsorption efficiency of 73% for 9 cycles. CHAUDHARY *et al.* [45], reported that gelatin grafted methyl methacrylate/graphite hydrogel composite for adsorption of methyl violet showed stability of 95.8% after 6 cycles. PRIYA *et al.* [46] described that the sodium alginate/gelatin-based ZnS-nanocomposite hydrogel for adsorption of bieberich scarlet and crystal violet dyes presented efficiency greater than 90% after 4 cycles for both dyes.

If we compare the adsorption and regeneration capacities obtained for composites based on commercial and residual gelatin at the end of the tenth cycle (Figure 3), there are reductions of 23 and 20% in the regeneration and adsorption capacity, respectively, of RCTLW gelatin compared to commercial gelatin. However, it must take into account that the residual origin of the recovered gelatin does not imply the use of commercial gelatin with favorable characteristics for food production, addressing a more technological and environmental bias [47].

#### 4 CONCLUSIONS

This work, the study of adsorption of the tartrazine yellow dye was presented through the equilibrium, kinetic and reuse tests. In the equilibrium tests, the commercial gelatin and RCTLW composite beads showed an adsorption capacity of 202.39 and 131.32 mg.g<sup>-1</sup>, respectively, estimated by the Langmuir model. For commercial gelatin/CNT's beads, the Freundlich model fitted better to the experimental data, indicating that the adsorption by the referred material is not limited to monolayer, whereas for RCTLW gelatin/CNT's beads, the Langmuir model better predicted the behavior of the isothermal curve, suggesting monolayer adsorption. In the adsorption kinetics, the density continued to increase after 300 min for both composite materials, with a better prediction of the pseudo-first order model.

In general, the gelatin composite beads showed a promising bet for use as an adsorbent for the tartrazine yellow dye. In comparison to commercial gelatin, even with lower capacities for adsorption and regeneration of the dye under study, RCTLW gelatin presents a more technological and environmental bias, allowing the use of compounds of interest, such as collagen, and minimizing the solid waste discarded to the environment.

As perspectives, we emphasize the need for works that aim at studies of the economic viability of gelatins from residual sources, such as tannery wastes, for example, for applications as an adsorbent.

#### 5 ACKNOWLEDGMENTS

The authors would like to acknowledge the Coordination for the Improvement of Higher Education Personnel (CAPES) – Finance Code 001, the National Council for Scientific and Technological Development (CNPq) – Proc. 409173/2018-5, Research Support Foundation of Rio Grande do Sul (FAPERGS) – Proc. 16/0258-4 and University of Passo Fundo (UPF) for their financial support in this research.

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