# BIOSORPTION EVALUATION OF SYNTHETIC DYE FROM FOOD INDUSTRY WASTEWATER ONTO SILKWORM COCOONS: PRELIMINARY STUDIES

DUSI G. G.<sup>A</sup>
CANTELI A. M. D.<sup>A</sup>
KARP J. R.<sup>A</sup>
MAFRA L. H.<sup>A</sup>
SCHEER, A. P.<sup>A</sup>
SILVA V. R.<sup>A</sup>

The aim of this study was to evaluate the synthetic azo dye (tartrazine) biosorption onto second line silkworm cocoons. Batch adsorption system was used to investigate the effect of pH and initial tartrazine concentration in the liquid phase. Also, the kinetic mechanism was investigated at 20°C and pH 2.0.The highest adsorption was obtained at the lowest pH evaluated, while the assays with pH above 3.0 did not show significant adsorption at the first hour of the process, indicating that biosorption is more favorable at lower values of pH. The adsorption kinetic was studied at pH 2.0andcompared with the kinetic mechanism of convective mass transfer and diffusion models. The kinetic behavior of biosorption process showed a high amount of dye adsorbed at the beginning of the process, however, after saturation of the functional groups, the adsorption rate decreased over time until saturation. After 24 hours of batch operation, the uptake of tartrazine onto silkworm cocoons was  $40.39~mg~g^{-1}$ , and the rate of adsorption reduces from  $3.430~to~0.003~mg~min^{-1}g^{-1}$ , suggesting that the process approaches the equilibrium. The Crank model provided the best fit. The results revealed that silkworm cocoons have the potential to be used as a biosorbent for wastewater treatment containing tartrazine.

KEYWORDS: SILKWORM COCOONS, TARTRAZINE, BIOSORPTION, BATCH ADSORPTION.

<sup>A</sup> CHEMICAL ENGINEERING DEPARTMENT, FEDERAL UNIVERSITY OF PARANÁ FRANCISCO H. SANTOS ST., CURITIBA, PARANÁ, BRAZIL

#### 1 INTRODUCTION

Synthetic dyes are worldwide applied in food and pharmaceutical industries as additives. Acid yellow 23, commonly referred as tartrazine, is one of the most employed synthetic dyes in the food industry to adjust the yellow and red colors of soft drinks, cake mixes, ice cream, candies, gelatins and cereals (Prado and Godoy, 2003; Kassem and El-Sayd, 2014). It has been reported that the ingestion of tartrazine may contribute to various immunologic responses and adverse effects of children and people with tartrazine intolerance (Moutinho *et al.*, 2007; Wang *et al.*, 2012). Furthermore, the food industry wastewater with dye content, even in low concentrations, may interfere with the passing of light, which causes adverse effects on the aquatic ecosystems that receive such discharges (Fernandes *et al.*, 2010).

The wastewater treatment usually applies chemical and physical methods (such as coagulation, nanofiltration, ion-exchange and electro-oxidation), however, these technologies are usually expensive or ineffective and can also present low applicability or adaptability to a wide range of dye containing wastewaters (Harrelkas *et al.*, 2009, Gilpavas *et al.*, 2016). As a viable alternative, biosorption has received increasing interest owing to its cost-effectiveness, less sludge production, and environmental friendliness, justifying the development of a practical bioprocess for dyecontaining wastewater (Srinivasan and Viraraghavan, 2010, Dotto *et al.* 2012, Ozbay *et al.*, 2013). Biosorption is the process of binding adsorbate on the surface of a biological material by physical affinity or chemical interaction of the adsorbate with the biosorbent functional groups such as the carboxyl, hydroxyl, amino, carbonyl, phosphate, and sulfonic groups (Podstawczyk *et al.*, 2015). In this context, natural fibers like the cocoons of silkworm *Bombyx mori* show great perspective.

The cocoons of silkworm caterpillars have evolved over millions of years to protect the larvae from predators during the vulnerable phase of worm-to-moth transformation. The cocoons themselves are a remarkable engineering composite structure that is built by the animals using a continuous dualstrand of silk fibroin (almost 1500 m in length) coated with hydrophilic protein sericin binder, maintaining the cocoon's structural integrity (Ude et al., 2014, Shah et al., 2015). However second-line silkworm cocoons are usually not used for the production of silk thread due to their visual defects (irregular sizes, irregular fiber thickness and stains in the surface of the cocoons). The cocoons of silkworm derived from Bombyx mori contain two major proteins: fibroin and sericin. Silk fibroin is a fibrous protein that corresponds to 70% of the cocoon weight, and its stiffness and strength comes from its crystalline structure comprising 17 amino acids, with predominant nonpolar amino acid groups (as glycine and alanine, with 32% and 40%, respectively) and polar amino acid serine (almost 20%) (Park et al., 2002); while sericin is a globular protein polymer, comprising of 18 amino acids, with predominant polar amino acid groups, as serine (25 %), acids aspartic (17 %), threonine (6%) and acid glutamic (5 %) (Takasu et al., 2002; Silva et al., 2016). These proteins showed applications in tissue engineering and biotechnology, as well as cosmetic and food industries (Zhang et al., 2006; Kundu et al., 2008; Zuge et al., 2017). Some studies have reported the applicability of these proteins in adsorption, endorsing their capacity to remove synthetic dyes and metals from wastewater (Aslani et al., 1998; Chen et al., 2011; Gimenes et al., 2016). In this context, this study focuses on the applicability of the second-line silkworm cocoon of Bombyx mori, on the adsorption of tartrazine in aqueous solution. To this aim, batch experiments were performed to investigate the adsorption kinetics of the process.

#### **2 MATERIAL AND METHODS**

## 2.1 BIOSORBENT

The biosorbent used in this study was the second line cocoons produced by domestic worm *Bombyx mori*, obtained from the northwest region of Paraná. The cocoonswere cut into small pieces, with an area of almost 1.0 cm<sup>2</sup>. The surface area was determined by the BET method (Brunauer *et al.*,

1938), with nitrogen adsorption/desorption measurements taken at 77.4 K using a Quantachrome<sup>™</sup> Autosorb<sup>-1</sup> instrument. The surface morphology was examined by scanning electron microscopy using a Jeol JSM-6360LV microscope. Tartrazine (Fig. 1, molecular formula C<sub>16</sub>H<sub>9</sub>Cl<sub>2</sub>N<sub>4</sub>Na<sub>3</sub>O<sub>9</sub>S<sub>2</sub>), was donated from Duas Rodas Company, Brazil. Concentrations of the aqueous dye solution were monitored on a spectrophotometer (FEMTO – model 600 plus) at a wavelength of 427 nm (Mittal *et al.*, 2007). The pH of the aqueous solution of the tartrazine dye was adjusted with 0.1 mol L<sup>-1</sup> HCl or 0.1 mol L<sup>-1</sup> NaOH. All chemicals were of analytical grade and were used without further purification.

FIGURE 1.CHEMICAL STRUCTURE OF TARTRAZINE.

#### 2.2 BATCH ADSORPTION STUDIES

The batch adsorption experiments were carried out in a temperature-controlled orbital shaker (Tecnal<sup>TM</sup> TE-421, Sorocaba, Brazil) at 150 rpm 20.0  $\pm$  0.5 °C. In each test, 50 mL of an aqueous solution of tartrazine was placed into a 125 mL hermetically sealed Erlenmeyer flask with 0.050  $\pm$  0.005 g of a previously sliced silkworm cocoon. The uptake of tartrazine at time t, q(t) (mg g-1), was obtained through the mass balance, according to equation 1:

$$q(t) = \frac{[Co - C(t)] \cdot V}{W}$$
 (Eq. 1)

Where V (mL) is the solution volume, Co (mg L<sup>-1</sup>) is the initial concentration of tartrazine, C(t)(mg L<sup>-1</sup>) is the liquid-phase concentration of tartrazine dye at time t (min) and w (g) is the mass of the biosorbent. The rate of tartrazine adsorption (dq(t)/dt) was evaluated by central finite differences between the experimental data.

# 2.3 EFFECT OF PH AND INITIAL CONCENTRATION OF TARTRAZINE ONTO BIOSORPTION PROCESS

The effects of pH and initial concentration of tartrazine on the liquid phase were evaluated in a batch process. The pH test was carried out for 1 hour at  $20^{\circ}$ C, with 50 mL of an aqueous solution of tartrazine with an initial concentration of 50 mg L<sup>-1</sup>, and  $0.050 \pm 0.005$ g of a silkworm cocoon. The pH was set between 2.0 and 8.0 and was adjusted with 0.1 mol L<sup>-1</sup> HCl or 0.1 mol L<sup>-1</sup> NaOH. The effect of the initial concentration of tartrazine on the biosorption was carried out for 24 hours at pH 2.0 and temperature of  $20^{\circ}$ C, with 50 mL of an aqueous solution of tartrazine and  $0.050 \pm 0.005$ g of silkworm cocoon, and the concentration of tartrazine in the liquid phase was set between 50 and 250 mg L<sup>-1</sup>.

## 2.4 KINETIC STUDIES

Kinetic studies of biosorption of tartrazine were made at the best pH previously evaluated, the temperature of  $20^{\circ}$ C, and initial tartrazine concentration of 50mg L<sup>-1</sup>and  $0.050 \pm 0.005$  g of a silkworm cocoon.

Five kinetic models were used to fit the experimental adsorption kinetics data, that is, the pseudo-first order, pseudo-second order, Weber-Morris intraparticle diffusion, external liquid diffusion, and Crank diffusion models. The pseudo-first order (eq. 2) and pseudo-second order (eq. 3) models assume that the adsorption mechanism is similar to the chemical reaction process (Ho and Mckay, 1999), where q(t) and  $q_{EQ}$  are, respectively, the amount of tartrazine adsorbed onto silkworm cocoon at time (t) and equilibrium, whereas  $K_1$  and  $K_2$  are, respectively, the kinetic constants of the pseudo-first order and pseudo-second order models:

$$\frac{dq(t)}{dt} = K_1 \cdot \left( q_{EQ} - q(t) \right)$$
 q(0)=0 (Eq. 2)

$$\frac{dq(t)}{dt} = K_2 \cdot (q_{EQ} - q(t))^2$$
 q(0) = 0 (Eq. 3)

The internal diffusion models used in this study were the Weber-Morris intraparticle diffusion (eq. 4) and Crank (eq. 5) models, where  $K_{WM}$  is  $K_{C}$  are the effective intraparticle diffusion coefficient of the Weber-Morris model and global mass transfer coefficient of the Crank model, respectively. As reported by Qiu *et al.* (2009) and Tan and Hameed (2017), these models consider that the restrictive adsorption mechanism involves the diffusion phenomena onto the adsorbent, where the Weber-Morris relates the intraparticle diffusion while the Crank model is derived from porous intraparticle diffusion derived from Homogeneous Solid Diffusion Model, forplane plate geometry.

$$q(t) = K_{WM} \cdot \sqrt{t} \tag{Eq. 4}$$

$$q(t) = q_{EQ} \cdot \left\{ 1 - \frac{8}{\pi^2} \cdot \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \cdot exp[-(2n+1)^2 \cdot K_C \cdot t] \right\}$$
 (Eq. 5)

Also, the external liquid film diffusion model was evaluated (Puranik *et al.*, 1999). This model is generally used to describe the mass transfer from the bulk of the liquid through the liquid film surrounding the solid surface (equations (6) and (7)), where C(t) and  $C_{l}(t)$  are the tartrazine concentration in the bulk solution and the liquid film surrounding the sericin surface, respectively, and  $K_{TM}$  is the convective mass transfer coefficient. The parameters  $K_{L}$  and  $K_{TM}$  are the equilibrium parameters, adopted Langmuir isotherm as the equilibrium model.

$$\frac{dC}{dt} = K_{TM} \cdot [C(t) - C_I(t)] \qquad C(0) = Co \qquad (Eq. 6)$$

$$\frac{dC_{I}}{dt} = \frac{V \cdot K_{TM}}{w \cdot q_{M} \cdot K_{I}} \cdot [1 + K_{L} \cdot C_{I}(t)]^{2} \cdot [C(t) - C_{I}(t)]$$
  $C_{I}(0) = 0$  (Eq. 7)

#### 2.5 STATISTICAL ANALYSIS

All experiments were carried out in triplicate. The variance analysis (ANOVA) was performed for the results obtained. Tukey's test was used to compare means with 5% significance level. The software StatSoft<sup>TM</sup> STATISTICA (version 8.0) was used for the statistical analysis. The Levenberg–Marquardt algorithm was employed as the interactive method. The parameters and predicted values for the external liquid film diffusion model were obtained by stochastic optimization of the simulated annealing algorithm in a computer routine run in Fortran Visual Compaq 6.6. The standard deviation (SD, eq. 8) and mean absolute percentage error (MAPE, eq. 9) were obtained to determine the

validity of the models, where and are the experimental and predicted values of mass of tartrazine adsorbed in biosorbent, respectively.

$$SD = \frac{\sum_{i=1}^{n} (q_{i} - \overline{q_{i}})^{2}}{n}$$
 (Eq. 8)

MAPE = 
$$\frac{\sum_{i=1}^{n} |q_{i} - \overline{q_{i}}| / \overline{q_{i}}}{n}$$
 (Eq. 9)

#### **3 RESULTS AND DISCUSSION**

#### 3.1 ADSORPTION STUDIES

The SEM images of silkworm cocoon (Figure 2a, b) showed a surface made by long filaments, constituted by the protein fibroin adhered by the protein sericin, making a network with large voids between the filaments. The images related to the structure of the filaments (Figure 2b) indicate a surface of cylindrical geometry, smooth and uniform, without the presence of pores in the silk fiber. The small fragments present onto the filament surface are sericin proteins.

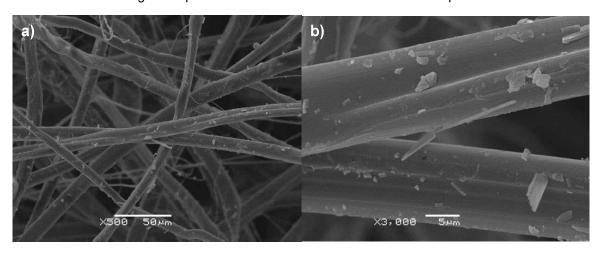


FIGURE 2. SCANNING ELECTRON MICROGRAPHS OF SILKWORM COCOON OF BOMBYX MORI. (A) X500; (B) X3,000

The BET analysis showed that the cocoon derived from *Bombyx mori* has a surface area of  $5.12 \text{ m}^2 \text{ g}^{-1}$  and pore volume of  $7.19 \times 10^{-2} \text{ cm}^3 \text{ g}^{-1}$ , indicating a nonporous morphology for the silk fiber. This behavior was expected; as the silkworm cocoon was made by a linear silk thread (fibroin) adhered by a globular protein (sericin).

The effect of pH on tartrazine dye adsorption onto silkworm cocoon of Bombyx mori was studied over a range of pH between 2.0 and 8.0, and the results are shown in Table 1. The highest adsorbed tartrazine mass obtained was with lower pH value, while at pH above 4.0 the tartrazine adsorption was minimal. A similar result was reported by Chen *et al.* (2012) and Silva *et al.* (2016), they observed that azo dyes adsorption onto sericin are favorable at pH below 3.0.This can be explained due to the interactions between the positive charges of the surface amino acids present in both proteins of the silkworm cocoons (such as the protonation of the amide groups (–NH<sub>2</sub>) and some polar amino acids as arginine (=NH<sub>2</sub><sup>+</sup>)) and the negative charge of the sulfonate group of the tartrazine dye (–SO<sub>3</sub><sup>-</sup>) (Chen *et al.*, 2012; Silva *et al.*, 2016).Therefore, the adsorption studies were conducted at pH 2.0.

# TABLE 1: EFFECT OF PH ON TARTRAZINE ADSORPTION ONTO COCOONS OF SILKWORM BOMBYX MORI.

рН	2.0	3.0	4.0	5.5	8.0
Mass of tartrazine adsorbed (mg g <sup>-1</sup> )*	$17.50 \pm 0.68^{\rm A}$	$10.50 \pm 0.68^{\rm B}$	$0.68\pm0.45^{\rm C}$	$0.68 \pm 0.20^{\circ}$	$0.41 \pm 0.15^{\rm C}$

<sup>\*</sup> Means with different letters represent statistical difference according to the Tukey's test (P < 0.05)

The effect of initial concentration of tartrazine in aqueous solution was studied over a range of tartrazine concentration, between 50 and250.0 mg L<sup>-1</sup>, at pH 2.0 during 24 hours, and the results are shown in Table 2. According to ANOVA assay, the initial concentration of tartrazine in aqueous solution has significant influence in the biosorption process with silkworm cocoons. As expected, an increase in the concentration in the aqueous phase promotes a raise in the mass transfer potential between the liquid phase and the surface of the silkworm cocoon, promoting a higher adsorption over a same period.

TABLE 2: EFFECT OF INITIAL CONCENTRATION OF TARTRAZINE IN THE ADSORPTION PROCESS WITH SILKWORM COCOONS

Initial concentration of tartrazine in aqueous solution (mg L <sup>-1</sup> )	50	100	150	200	250
Mass of tartrazine adsorbed (mg g <sup>-1</sup> )*	$40.39 \pm 0.82^{\rm D}$	$53.54 \pm 0.54^{\rm C}$	$58.36 \pm 2.02^{\text{B}}$	$60.88 \pm , 1.74^{\rm A,B}$	$63.71 \pm 1.60^{\text{A}}$

<sup>\*</sup> Means with different letters represent statistical difference according to the Tukey's test (P < 0.05)

The highest tartrazine mass adsorbed was obtained for the initial concentration of tartrazine of 250 mg L<sup>-1</sup>, but the amount of tartrazine adsorbed onto silkworm cocoon was not statistically different from an initial concentration of 200 mg L<sup>-1</sup>according to with Tukey's test with p < 0.05. These results could be suggested that tartrazine adsorption occurs preferentially in the functional groups (polar amino acids of sericin and fibroin, as aspartic acid, glutamic acid, threonine, and serine) until approaches their saturation. After 24 hours of biosorption process continues slowly probably due to the tartrazine adsorption at the non-selective sites of silkworm cocoons (as the non-polar amino acids, such as alanine and glycine).

#### 3.2 ADSORPTION KINETICS

The kinetics of the adsorption of tartrazine onto silkworm cocoon of *Bombyx mori* was measured through the curve of the adsorption capacity ( $q_t$ ) as a function of time (Figure 3 and 4). As reported in the literature (Aslani *et al.*,1998; Chen *et al.*, 2012; Gimenes*et al.*, 2016), the biosorption process with proteins derived from silkworm cocoons is more efficient at lower temperatures, so the adsorption kinetic study was developed at room temperature (20°C).

Table 3 reports the adsorption velocity (dq<sub>t</sub>/dt) and the decay rate of tartrazine concentration in the liquid phase. Adsorption of tartrazine onto silkworm cocoon showed to be higher during the first hours of contact; however, after 3 hours the adsorption rate presented high decrease overtime. Within the first 6 hours, approximately, 73.9 % of tartrazine was adsorbed from an aqueous solution containing 50 mg L<sup>-1</sup> of the azo dye. The difference between the amount of tartrazine removed from solution at 6 and 24 hours was less than 6.92%, but the adsorption rate was reduced from 0.021 to 0.003 mg g<sup>-1</sup> min<sup>-1</sup>, indicating a reduction of 85.4 % of adsorption velocity. Although it is observed that the silkworm cocoon still has the capacity to adsorb tartrazine, after 24 hours, it's suggested that the biosorption process approaches the steady-state. The adsorption rate reduces continuously due to the reduction of the mass transfer potential between the liquid phase and the solid as well as the diminution of the active sites of the biosorbent.

TABLE 3: RATE OF TARTRAZINE ADSORPTION AND PERCENTAGE OF TARTRAZINE REMOVED FROM LIQUID PHASE AT PH 2.0 AND 20°C.

Time (min)	2	10	30	60	90	180	360	1440
Velocity of adsorption process (dq <sub>r</sub> /dt) (mg g <sup>-1</sup> min <sup>-1</sup> )	3.430	0.412	0.277	0.169	0.127	0.094	0.021	0.003
Percentage of tartrazine removed form liquid phase (%)	13.8	20.8	31.8	40.6	45.1	66.4	73.9	80.8

Silva et al. (2016) evaluated the biosorption of the synthetic azo dye Bordeaux S onto sericin powder (obtained directly from silkworm cocoons of Bombyx mori), and the authors related the kinetic approaches the equilibrium near 1.0 hour, at pH 2.0 and 20°C, resulting in a mass of azo dye adsorbed of almost 200 mg g<sup>-1</sup>, much higher than obtained with silkworm cocoon. Although the silkworm cocoon has lower adsorption capacity than pure sericin powder, it has the advantage of direct application as biosorbent, while to obtain pure sericin powder is necessary a degumming step (sericin extraction with hot water and alkalis as Marseille soap, with temperatures above 100°C), purification (as centrifugation, ultrafiltration and nanofiltration) and freeze-drying processes (Capar et al., 2008; Chen et al., 2012). Adopted natural silkworm cocoon as biosorbent for the treatment of food industry wastewater reduces the cost of adsorbent, instead of the use of the processed silk proteins as sericin powder or fibroin silk fiber.

#### 3.3 KINETICS OF ADSORPTION IN BATCH OPERATION

Table 4 reports the kinetic parameters of the tartrazine adsorption onto silkworm cocoon, while Figures 3 and 4 showed the kinetic adjusted models and the deviation between the predicted and experimental values measured. It was observed that the Crank diffusion model provided the best fit with the experimental data, with the lowest values of SD (2.35) and MAPE (0.15).

At the beginning of the process, the adsorption rate is high due to the presence of surface charges, promoting favorable interaction between the functional groups of silkworm cocoon and tartrazine at pH 2.0, the interaction is specific and favorable, so that tartrazine mass transferred between the liquid phase (inside in the voids of the cocoon's network structure) until the surface of the silk fiber is the major mass transfer resistance. In this case, the Crank model based on theory of Homogeneous Solid Diffusion showed to be more representative of the adsorption process. As illustrated in Figures 3 and 4, the major errors of the fitted models are in this initial step, except for the Crank model.

After the functional groups are filled with tartrazine, the adsorption process until occurs, probably due the interaction between tartrazine and non-selective sites of the silk fiber. Diffusion effects associated with the reduction of mass transfer potential (due to the diminution of the amount of tartrazine in the liquid phase) promotes the reduction of the rate of the adsorption process.

The Weber–Morris model provided very high values of SD (84.66) and MAPE (0.88), and as shown in Fig. 4a and 4b, this model did not describe the adsorption process of tartrazine onto silkworm cocoon. This model considers the intraparticle diffusion, but as Figure 2 and BET analysis showed, the silkworm cocoon fibers are nonporous structure, what suggests that the internal mass transfer (inside the fiber structure) is not a relevant resistance mechanism to the adsorption process.

TABLE 4: KINETIC PARAMETERS OF TARTRAZINE ADSORPTION ONTO SILKWORM COCOON.

Kinetic models	Parameters				
_	K <sub>1</sub> x 10 <sup>+2</sup> (min <sup>-1</sup> )	1.25± 0.19 40.39± 0.83 13.42			
First order	q <sub>EQ</sub> (mg g <sup>-1</sup> )				
First order	SD				
	MAPE	0.996			
_	K <sub>2</sub> x 10 <sup>+4</sup> (g mg <sup>-1</sup> min <sup>-1</sup> )	5.64 ± 0.78			
Second order	q <sub>EQ</sub> (mg g <sup>-1</sup> )	40.39 ± 0.83			
Second order	SD	6.60			
-	MAPE	0.458			
	Kw (mg g <sup>-1</sup> min <sup>-0.5</sup> )	1.48 ± 0.21			
eber-Morris diffusion	SD	84.66			
_	MAPE	0.878			
	$K_{c}(min^{-1}) \times 10^{+3}$	8.82 ± 0.54			
Crank diffusion -	q <sub>EQ</sub> (mg g <sup>-1</sup> )	40.39 ± 0.83			
Crank diffusion -	SD	2.35			
_	MAPE	0.15			
	K <sub>TM</sub> (min <sup>-1</sup> ) x 10 <sup>+3</sup>	9.43			
-	Q <sub>MAX</sub> (mg g <sup>-1</sup> )	64.84			
ternal liquid diffusion	K <sub>L</sub>	0.125			
-	SD	12.92			
-	MAPE	1.07			

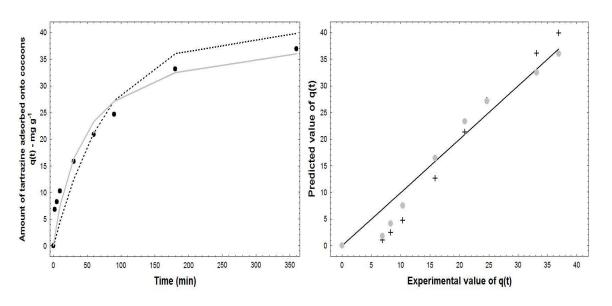


FIGURE 3.KINETIC OF TARTRAZINE BIOSORPTION ONTO SILKWORM COCOON: (A) EXPERIMENTAL DATA (•), PSEUDO-FIRST ORDER (---) AND PSEUDO-SECOND (—) ORDER MODELS. (B) PREDICTED VALUES VERSUS EXPERIMENTAL DATA, PSEUDO-FIRST ORDER (+) AND PSEUDO-SECOND ORDER (•).

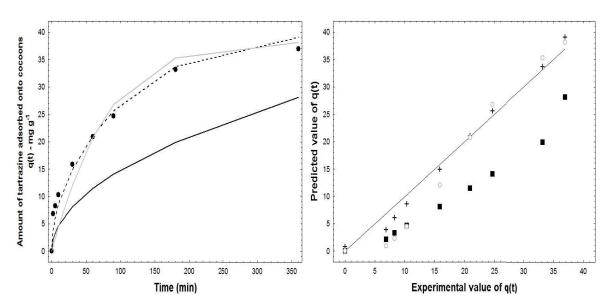


FIGURE 4.KINETIC OF TARTRAZINE BIOSORPTION ONTO SILKWORM COCOON: (A)

EXPERIMENTAL DATA (●), WEBER-MORRIS (─), CRANK (---), EXTERNAL LIQUID DIFFUSION (─).

(B) PREDICTED VALUES VERSUS EXPERIMENTAL DATA FOR WEBER-MORRIS (■), CRANK (+)

AND EXTERNAL LIQUID DIFFUSION (○).

The pseudo-first order and pseudo-second order models showed large deviations in the prediction of tartrazine adsorption values at the beginning of the process (Fig. 3a and 3b), tending to underestimate the experimental values observed, as the external liquid diffusion model. These models did not consider the mass transfer resistance between the liquid phase (inside the voids of the cocoon's network structure) and the surface of the silk fiber. After the tartrazine filled the functional groups, the adsorption rate decreases due: the reduction of the sites available for adsorption and the diminution of mass transfer potential between the liquid phase and silk fiber surface. The kinetic adsorption process approaches at linear driving force, which can be explained by other models, as the external liquid diffusion and pseudo-second order models.

### CONCLUSION

The adsorption process is favorable at pH below 3.0, due to the interaction between the positive surface charge of the functional groups of silkworm cocoon and negative charge of the sulfonate groups of the tartrazine dye.

The kinetic study showed higher adsorption rate at the first hours, and after 3 hours the adsorption rate presented high decrease overtime.

The Crank model provided the best fit with the lowest values of SD (2.35) and MAPE (0.15). The results of this study revealed that silkworm cocoons have potential for the treatment of food industry wastewater containing tartrazine

#### **RESUMO**

# AVALIAÇÃO DA BIOSSORÇÃO DE CORANTES SINTÉTICOS, PRESENTES EM EFLUENTES DA INDÚSTRIA DE ALIMENTOS, EM CASULOS DO BICHO DA SEDA: ESTUDOS PRELIMINARES.

O objetivo deste estudo foi avaliar a biossorção de corante sintético (tartrazina) em casulos de bicho da seda de segunda linha. Foi utilizado um sistema de adsorção em batelada para avaliar o efeito do pH e da concentração inicial de tartrazina na fase líquida. Além disso, o mecanismo

cinético foi investigado a 20°C e pH 2.0. A máxima adsorção foi obtida no menor pH avaliado, enquanto os ensaios com pH acima de 3.0 não apresentou adsorção significante durante a primeira hora do processo, indicando que a biossorção é mais favorável em valores mais baixos de pH. A cinética da adsorção foi comparada com mecanismos cinéticos com modelos de transferência de massa e de difusão convectiva. O comportamento cinético do processo de biossorção apresentou uma grande quantidade de corante adsorvida no início do processo, contudo, após a saturação dos grupos funcionais do biossorvente, a taxa de adsorção diminuiu ao longo do tempo até a saturação. Após 24 horas de operação em batelada, a captação da tartrazina nos casulos foi de 40.39 mg g<sup>-1</sup>e a taxa de adsorção reduziu de 3.430 a 0.003 mg min<sup>-1</sup> g<sup>-1</sup>, sugerindo que o processo aproxima-se do equilíbrio. O modelo de Crank forneceu o melhor ajuste. Os resultados mostraram que os casulos do bicho da seda têm potencial para serem usados como biossorventes para tratamento de efluentes contendo tartrazina.

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