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CONSTRUCTION AND EVALUATION OF A CSTR REACTOR FOR THE TREATMENT OF TEXTILE EFFLUENTS

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Abstract: The textile industry, which is influential in the Brazilian economy, generates effluents that cause various environmental impacts when discharged into water bodies, altering the color, transparency, pH and temperature of the water, damaging the photosynthesis of aquatic plants and, consequently, marine life. In addition, they compromise the ecological balance, exacerbating the damage to the environment. A common example is eutrophication, caused by excess nutrients in effluents, which stimulates excessive algae growth, reducing oxygen levels. It is therefore essential to continue investigating alternative methods to reduce pollution and ensure sustainability in the textile sector. Therefore, this study investigated the kinetics of the reaction between the Crystal Violet dye and NaOH in a CSTR reactor, built by the authors, with the aim of determining the reaction's rate constant, evaluating its order, determining the system's conversion and the model that best describes it. In this way, the integral and equally spaced points methods were implemented, respectively, to define the kinetic rate constant of the reaction and its order, and, in the end, the pseudo-first order kinetics methodology was used, since the reaction was monitored using the Crystal Violet reagent. To help monitor the behavior of the reaction, a computer model of the system was proposed, from time 0 to 25 min, which showed the height and volume profiles of the CSTR and the concentrations of the reagents. The time conversion of the system, obtained experimentally, was significant, reaching 81.84%, which attests to the efficiency of the system. In order to better describe the CSTR reactor and represent a real system, approaches such as segregation, tanks in series, dispersion, ideal models and CSTRs with dead zones were considered preferential channels. Finally, the results indicated that the series tank model best describes the reactor.

Keywords: Chemical Kinetics, Agitated Mixing Tank Reactor, Effluents, Crystal Violet, Modeling.

INTRODUCTION

The textile industry plays a crucial role in the Brazilian economy, according to data from the Brazilian Textile Industry Association - ABIT (2018), but its operations generate effluents which, when disposed of inappropriately, cause serious environmental impacts. These effluents alter the color, transparency, pH and temperature of the water, compromising the photosynthesis of aquatic plants and, consequently, marine life (NUNES, 2004). One of the most talked about problems is eutrophication, which occurs due to the excess nutrients present in effluents, leading to excessive algae growth and, consequently, a reduction in oxygen levels in the water (Dotto & McKay, 2020).

Brazilian legislation, through CONAMA Resolution No. 430/2011, establishes strict standards for the discharge of effluents into water bodies, with the aim of preserving water quality and environmental balance. The general procedure is to use a combination of physical-chemical and biological processes to treat these effluents, adapting the methods to the specific characteristics of the pollutants (BELTRAME, 2000). However, the presence of dyes in textile industry effluents represents a particular challenge (NUNES, 2019). In this context, as the imbalance in the aquatic ecosystem grows, the urgency to develop new methods of effluent treatment, promoting sustainability in the textile sector, increases.

The design of a mixing reactor is directly linked to the evaluation of a chemical method in relation to its economic viability, using the selection of raw materials and the analysis of the results of each stage, which according to Levenspiel (2000), among all the stages necessary for the formation of a product,

chemical treatment is the main part of the process and is responsible for the success or failure of this evaluation.

In these the last few decades have also seen progress in the development of experimental determination of the distribution of residence times in tanks and reactors (SASSAKI, 2005), so in this project, various ways were used to determine the residence time in the reactor in order to have greater certainty in the data obtained.

The crystal violet dye, which has various applications such as DNA analysis and cell and tissue research, is also widely used in the textile industry to dye fabrics. However, due to its toxicity, it is necessary to treat the effluent, one of the treatment routes being the use of caustic soda, in which there is a process of denaturation of the dye and its partial neutralization, since the disposal of dyes in wastewater that generates low concentrations causes blockage of the passage of light affecting aquatic life and can cause bioaccumulation and biomagnification (SILVA F., 2015). Generally, dyes are resistant to degradation and are not biodegradable (SHARMA et al., 2019). In addition, the reaction of crystal violet and caustic soda tends to form by-products that are less toxic than the violet itself.

Therefore, the main objective of this study is to explore the kinetics of the reaction between the Crystal Violet dye and NaOH in a CSTR reactor set up by students at the Federal University of the Triângulo Mineiro (UFTM), in order to determine the reaction rate constant and evaluate its order using different methods. In addition, the aim is to analyze the reactor's performance, comparing the conversion results obtained through experimental practice with the theoretical reference predictions, seeking the model that best represents the system.

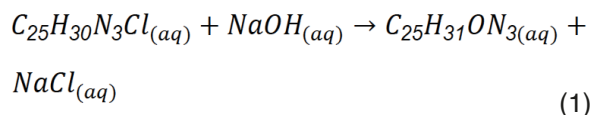
LITERATURE REVIEW

HYDROLYSIS OF CRYSTAL VIOLET DYE

Crystal violet (VC) is a basic cationic triphenylmethane dye that is widely used in medical and forensic fields, and especially in the textile industry as a synthetic dye (ADAK et al., 2005). This dye, like others based on triphenylmethane, poses a potential risk to aquatic and terrestrial life, and can induce tumor growth in some species of fish, as well as acting as a mitotic and clastogenic poison (MANI; BHARAGAVA, 2016).

In addition, VC is environmentally persistent and cannot be removed by traditional methods such as filtration, precipitation, adsorption and electro dialysis, due to its synthetic nature (GANEVA et al., 2021).

In aqueous solution, VC dissociates into $C_{25}H_{31}ON_3^+$ and Cl^- , generating a violet solution. The cation formed reacts strongly with OH^- , producing colorless carbinol, according to equation 1 (SALAHUDEEN; RASHEED, 2020):



The evolution of the reaction can be monitored according to the loss of color of the dye solution, until it becomes colorless. The reaction rate ($-r_A$) is given according to Equation 2 (SALAHUDEEN; RASHEED, 2020; CONCEIÇÃO; DIOGO, 2013):

$$-r_A = \frac{-dC_A}{dt} = kC_A^a C_B^b \quad (2)$$

Where:

$-r_A$: overall rate of the reaction;

k: reaction rate constant;

C_A^a : C concentration of crystal violet raised to its stoichiometric coefficient;

C_B^b : C concentration of sodium hydroxide raised to its stoichiometric coefficient;

Considering that the concentration of sodium hydroxide is in excess, its decay will be negligible. In this case, crystal violet is the limiting reagent and the rate equation can be rewritten according to Equations 3 and 4.

$$-r_A = \frac{-dC_A}{dt} = k'C_A^a \quad (3)$$

$$k' = kC_B^b \quad (4)$$

Where:

k' : pseudo-first order constant;

CONTINUOUS STIRRED TANK REACTOR (CSTR) DESIGN

The continuous stirred tank reactor (CSTR) or retromixing reactor is mainly used for liquid phase reactions. It is generally operated in a stationary regime and is considered to be perfectly mixed, so the temperature, concentration or reaction speed do not depend on time or position, meaning that these variables remain constant inside the reactor. Consequently, their values at the reactor outlet are the same as those inside (FOGLER, 2002).

Considering Equation 5 as the general molar balance equation (Fogler, 2002):

$$v_{A0} - v_A + \int_0^V r_A dV = \frac{dN_A}{dt} \quad (5)$$

To solve the equation, it is assumed that there is no accumulation or variation in volume; therefore, the balance is reduced to Equation 6, obtaining the design equation for the CSTR reactor.

Where:

V: reactor volume;

$$V = \frac{v_{A0} - v_A}{-r_A} \quad (6)$$

v_{A0} : molar input flow rate of species A [mol/t];

v_A : molar outflow rate of species A [mol/t];

You can relate v_A and the conversion (X) using Equation 7.

$$v_A = v_{A0} - v_{A0}X \quad (7)$$

Substituting (7) into (6) and making the necessary simplifications gives the volume of the CSTR as a function of conversion using Equation 8.

$$V = \frac{v_{A0}X}{-r_A} \quad (8)$$

MATERIALS AND METHODS

MATERIALS

Materials		
Glass jug with stand metal (5.5 L);	Analytical balance;	Glass vats;
Crystal violet;	Crystal violet solution (3x10 ⁻⁵ mol/L);	VIS UV- spectrophotometer;
2 macrotip serum bottles with choke;	Crystal violet solutions for building the calibration curve (0.3, 0.6, 1.5 and 3.0x10 ⁻⁵ mol/L);	Magnetic stirrer; Universal support;
2 plastic bottles;	Sodium hydroxide P.A.;	Burette jaws;
2 metal clamps;	Sodium hydroxide solution (0.05 mol/L);	Stopwatch;
Bench-top mechanical stirrer;	Thermometer;	Beakers.
MDF stand with wheels;	10 mL pipette;	

Table 1 - Materials used in the study

Source: Authors, 2024.

CRYSTAL VIOLET CALIBRATION CURVE

To construct the crystal violet calibration curve, solutions were prepared with concentrations of 0.3, 0.6, 1.5 and 3.0 x 10⁻⁵ mol/L. The solutions were made by diluting a 1 g/L crystal violet stock solution in distilled water, resulting in a final volume of 100 mL for each concentration.

In the spectrophotometer, aliquots of each solution were transferred to quartz cuvettes and the absorbance was measured at 595 nm, the wavelength value described by Du

et al. (2013). The absorbance values obtained were plotted on an Absorbance versus Concentration graph. The equation of the linear regression line was determined to relate the data obtained, allowing the concentration of crystal violet in future samples to be quantified.

DETERMINATION OF THE REACTION SPEED CONSTANT (K)

100 mL of a crystal violet solution with a concentration of 3.0 x 10⁻⁵ mol/L was added to a beaker. The solution was kept under constant stirring and the temperature was checked to ensure controlled conditions. Quickly, 100 mL of a NaOH solution was added to the crystal violet solution and the timing started immediately. The concentration of NaOH used was sufficient to ensure a pseudo-first order condition, where the concentration of NaOH is significantly higher than that of the crystal violet.

Samples of 10 mL were taken from the reaction medium at times 2, 4, 6, 8, 10, 15 and 20 minutes and these were transferred to cuvettes and immediately analyzed in the spectrophotometer at 595 nm to measure the absorbance. After reading, the entire volume of each sample was returned to the reaction medium to keep the volume constant.

The absorbance values obtained were used to calculate the concentrations of crystal violet remaining at each time point, using the previously determined calibration curve equation. From the concentration data over the time, a curve was constructed to determine the kinetics of the reaction.

Applying the integral method according to Fogler (2009), it was possible to calculate k for orders 0, 1, 2 and 3, from Equations 9, 10, 11 and 12, respectively.

$$C_A = C_{A0} - kt \quad (9)$$

$$\ln(C_A) = \ln(C_{A0}) - kt \quad (10)$$

$$\frac{1}{c_A} = \frac{1}{c_{A0}} + kt \quad (11)$$

$$\frac{1}{c_A^2} = \frac{1}{c_{A0}^2} + 2kt \quad (12)$$

In addition, the method of equally spaced points was used to calculate k, according to equations 13, 14 and 15.

$$\frac{dc_A}{dt} \Big|_{t_0} = \frac{-3c_A + 4c_{A1} - c_{A2}}{2\Delta t} \quad (13)$$

$$\frac{dc_A}{dt} \Big|_{t_{1,2,m}} = \frac{c_{An+1} - c_{An-1}}{2\Delta t} \quad (14)$$

$$\frac{dc_A}{dt} \Big|_{t_n} = \frac{c_{An-2} - 4c_{An-1} + 3c_{An}}{2\Delta t} \quad (15)$$

MODELING THE CSTR REACTOR

With the reaction rate constant (k) determined, a simulation was carried out using the free software *Scilab* to determine the behavior of the height and volume of the CSTR and the concentrations of the reactants. The system studied, as well as its components, are shown in Figure 1 and, finally, its reaction and rate, as shown in Equation 1 and Equation 2 previously presented.

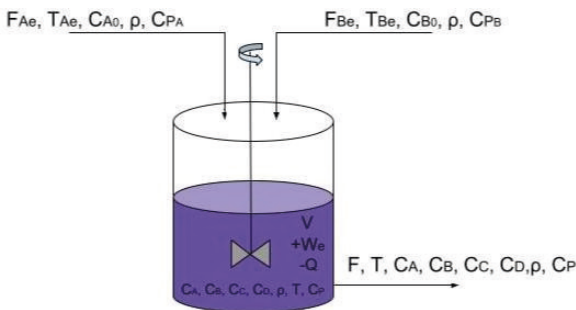


Figure 1: Modeling in the CSTR.

Source: Authors, 2024.

In this way, the overall mass balance and the mass balance by component were calculated to make up the equation used to build the simulation code, with the component C_A being crystal violet and C_B being NaOH, which are shown in Equations 16, 17 and 18. The following assumptions were made: the container (tank) is a perfect cylinder, assuming

that the mixture is also perfect, and finally, the physical properties are equal and constant. It is worth noting that the volume monitoring was adapted from Equation 16, in which the area term (A) is returned by multiplying the variable h, resulting in the volume variable (V).

$$\frac{dh}{dt} = \frac{(F_{Ae} + F_{Be}) - F}{A} \quad (16)$$

$$\frac{dc_A}{dt} = \frac{F_{Ae} \cdot c_{Ae} - (F_{Ae} + F_{Be})c_A}{A \cdot h} - kC_A \cdot C_B \quad (17)$$

$$\frac{dc_B}{dt} = \frac{F_{Be} \cdot c_{Be} - (F_{Ae} + F_{Be})c_B}{A \cdot h} - kC_A \cdot C_B \quad (18)$$

The initial conditions used were: initial height of 1.4 dm, initial volume of 2.5 L and initial concentration of 3.0×10^{-5} mol/L for crystal violet; 0.05 mol/L for NaOH. The system variables have the following units: $[F_i] = \text{dm}^3/\text{min}$; $[C_i] = \text{mol}/\text{dm}^3$; $[A] = \text{dm}^2$; $[h] = \text{dm}$, $[V] = \text{dm}^3$ and $[k] = \text{dm}^3/\text{mol} \cdot \text{min}$.

SYSTEM ASSEMBLY

An MDF stand with wheels was made to make it easier to move the system. A suqueira was placed on the support and used as a reactor to make the flow of the crystal violet and NaOH solutions, two equipments with flow control were used. These solutions were stored in two PET bottles with the bottom cut off and attached to the support with metal clamps.

A mechanical stirrer was positioned on an additional support, with the propeller centered inside the reactor to ensure homogeneous mixing during the reaction. The equipment tubes were attached to the reactor lid through holes drilled in the sides of the lid, allowing for the controlled addition of reagents. Beakers were positioned close to the reactor outlet tap, making it easier to take samples at the specified times. To better visualize the complete system, a drawing was made using *SketchUp* software, and the system was assembled as shown in Figure 2.

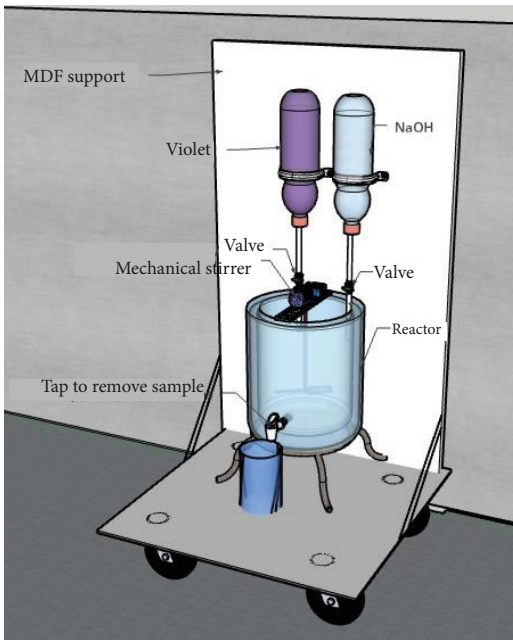


Figure 2: Representative and real scope of the system respectively.

Source: Authors, 2024

FLOW TESTS

After assembling the system, flow tests were carried out using water with different settings on the equipment throttles. The collection beakers were weighed beforehand and the fluid was collected over a period of 60 seconds, with all flow measurements carried out in triplicate. In addition, a continuous operation experiment was carried out on the reactor, adjusting the flow rates so that the fluid flow into the reactor was equal to the flow out, ensuring continuous operation of the reactor.

EXPERIMENTAL TESTS WITH THE CSTR

For the tests with the continuous CSTR, NaOH and violet solutions were prepared.

crystal. 4 L of NaOH solution and 6.5 L of crystal violet were made, with 2.5 L of NaOH previously allocated to the reactor. The bottles were then fed with the reagents, the stirrer was set to speed three and the samples were collected at the outlet over a period of 25 minutes.

The samples collected were sent to the spectrophotometer to determine the absorbance of the medium and, from this, the output concentration. The theoretical residence time, the DTR function, the area under the curve and the error in %, which is related to the actual residence time of the system, were calculated in Equations 19, 20, 21 and 22, respectively.

$$\tau_{teo} = \frac{V_{CSTR}}{F} \quad (19)$$

$$F(t) = \frac{C_i - C_0}{C_{\infty} - C_0} \quad (20)$$

$$\int_{t_0}^{t_1} f(t) dt = \frac{h}{2} [f(t_0) + f(t_1)] \quad (21)$$

$$Error (\%) = \frac{|\tau_{teo} - \tau_{real}|}{\tau_{real}} \times 100 \quad (22)$$

RESIDENCE TIME DISTRIBUTION (RTD) CALCULATIONS AND CONVERSIONS

Equation 23 was used to calculate the conversion per time for each of the points collected, where C_{VC_i} represents the initial concentration of Crystal Violet and $C_{VC}(t)$ the concentration obtained during the times collected.

$$x = \frac{C_{VC_i} - C_{VC}(t)}{C_{VC_i}} \quad (23)$$

The data was adjusted and the system conversion calculated using the Residence Time Distribution (RTD), using the segregation, serial tank and dispersion methods, so it was necessary to obtain the 1st and 2nd moment of the RTD, according to Equations 24, 25 and 26.

$$E(t) = \frac{c(t)}{\int_0^{\infty} c(t) dt} \quad (24)$$

$$t_m = \int_0^{\infty} tE(t) dt \quad (25)$$

$$\sigma^2 = \int_0^{\infty} (t - t_m)^2 E(t) dt \quad (26)$$

With the parameters calculated, it was possible to use the segregation methods, present in Equation 27, and serial tanks, available in Equations 28, 29 and 30.

$$X(t) = \frac{C_{B0}kt}{1 + C_{B0}kt} \quad (27)$$

$$n = \frac{\tau^2}{\sigma^2} \quad (28)$$

$$\tau_i = \frac{\tau}{n} \quad (29)$$

$$x = 1 - \frac{1}{(1 + \tau_i k)^n} \quad (30)$$

It is worth noting that the segregation model considers that the fluid flow passes through the reactor as a continuous series of globules, which retain their age, i.e. they do not exchange mass with the others. Thus, this type of behavior allows us to consider that each of the globules behaves like a small batch reactor.

The series tank model proposes the use of ideal mixing tanks in series in order to represent the behavior of an ideal reactor.

The dispersion method was then used, according to the following equations:

$$\frac{\sigma^2}{\tau^2} = \frac{2}{Pe_r} - \frac{2}{Pe_r^2} (1 - e^{-Pe_r}) \quad (31)$$

$$q = \sqrt{1 + 4Da/Pe_r} \quad (32)$$

$$x = \frac{4qe^{Pe_r/2}}{(1+q)^2 e^{Pe_r q/2} - (1-q)^2 e^{Pe_r q/2}} \quad (33)$$

$$Da = \frac{kC_{A0}C_{B0}V}{FC_{A0}} = \tau k C_{B0} \quad (34)$$

The dispersion model is generally used to describe non-ideal reactors, taking into account axial dispersion, which is governed by an expression analogous to Fick's Law of Diffusion. It is most commonly used to evaluate non-ideal PFR reactors.

Still within the conventional methods of obtaining the conversion, the equation of the ideal models for calculating the conversion was used, present in Equations 35, 36 and 37, shown for the particular system of the project in question.

$$C_A = C_{A0}(1 - X) \quad (35)$$

$$C_B = C_{B0}(\theta_B - \frac{b}{a}X) \quad (36)$$

$$V = \frac{(C_{A0}X + (X-1)C_{B0})F_{Ae} + (C_{B0}X + (X-1)C_{A0})F_{Be}}{kC_A C_B} \quad (37)$$

Finally, we looked for a model for the CSTR that included dead zones in its equation, since the system indicated has this deficiency; equations 38, 39, 40, 41, 42 and 43 were therefore used, according to Fogler (2009).

$$C_{As}(t) = C_{A0} - C_{A0} \left[1 - \left((1 - \beta) \cdot e^{-\frac{(1-\beta)(t)}{\alpha}} \right) \right] \quad (38)$$

$$C_{As} = \frac{C_{A0}}{\tau_s C_{Bs} k - 1} \quad (39)$$

In which:

$$\tau_s = \frac{V_s}{F_s} = \frac{\alpha V}{(1-\beta)F_{Ae}} \quad (40)$$

$$C_A = \frac{F_{Ae} - F_s}{F_{Ae}} \cdot C_A + \frac{F_s}{F_{Ae}} C_{As} \quad (41)$$

In which:

$$F_s = (1 - \beta)F_{Ae} \quad (42)$$

$$x = 1 - \frac{C_A}{C_{A0}} \quad (43)$$

This method approximates the behavior of a real reactor to a combination of an ideal CSTR, a dead zone volume and a *bypass* type detour; this combination is used since it approximates the behavior of the CSTR, which will present dead zones in which there will be no ideal mixing and the formation of preferential channels.

RESULTS AND DISCUSSIONS

CALIBRATION CURVE AND DETERMINATION OF THE REACTION VELOCITY CONSTANT (K)

To determine the reaction rate constant, the calibration curve for the crystal violet concentration was first constructed in the laboratory. From a known solution of 1 g/L was diluted to 4 solutions of 100 ml. Methods for determining k and order were then used to estimate the reaction kinetics. The method of equally spaced points **Figure 3** and the integral method were considered. The reaction behavior was treated as pseudo-first order, in which the experiment was conducted with crystal violet as the limiting reagent and $\text{NaOH}_{(aq)}$ in excess.

It was noted that the kinetic constant of the reaction had high variability considering the analysis from time 0 to 20 (min), where for the first calculation we considered up to time 10 min time variation $\Delta t = 2$ min and from point 10 to 20 $\Delta t = 5$ min, where point 10 was treated as the first point in this interval (**Figure 3(b)**). In order to obtain strictly equal spacings, we determined the k' corresponding to the interval 0 to 10 (min) with $\Delta t = 2$ min (**Figure 3(c)**). Subsequently, the absorbance between times 0 and 10 (min) was interpolated in order to obtain the absorbance of time 5

and calculate the interval 0 to 20 (min) with equal spacing of 5 minutes (**Figure 3(d)**). The results obtained indicated a high sensitivity of the kinetic constant, closer to the 3rd order. As a result, this method proved ineffective for understanding the kinetic constant of this reaction.

After obtaining unsatisfactory results using the equally spaced points method, it was necessary to apply the integral method, which can be seen in **Figure 4** below:

Figure 4 (b) shows the kinetic constant $k'=0.124 \text{ min}^{-1}$, which shows the second order $k=2.36 \text{ (L/mol.min)}$ and the equation for obtaining the reaction kinetics with the coefficient of determination (r^2) of the data obtained, where $r^2 = 0.73$ was observed. The fit by this method does not represent the best r^2 for the order assumption 1, however, in the case of this experiment, the use of order is a consequence of the reaction characteristic.

By obtaining the kinetic constant using the integral method and checking the sensitivity of k' to a higher order, the kinetics obtained using the pseudo-first order integral method guided what will happen in the CSTR reactor at steady state. The error associated with the kinetics of the reaction in the operation of the batch test was admitted, as a result of the unsatisfactory r^2 , and instability was observed in the reaction, i.e. after collecting the concentrations at the respective times, a change in tone was observed, becoming more transparent, which implies that the reaction requires a longer residence time than that for reagent consumption and product formation. The continuity of the reaction showed that carbinol will continue to be formed as long as the stoichiometry is met, and that the output ducts of this product will function with the properties of a PFR reactor and fillers will increase the residence time, favoring the formation of the desired product. It was observed that the reaction will be treated in a manner analogous to gray box modeling.

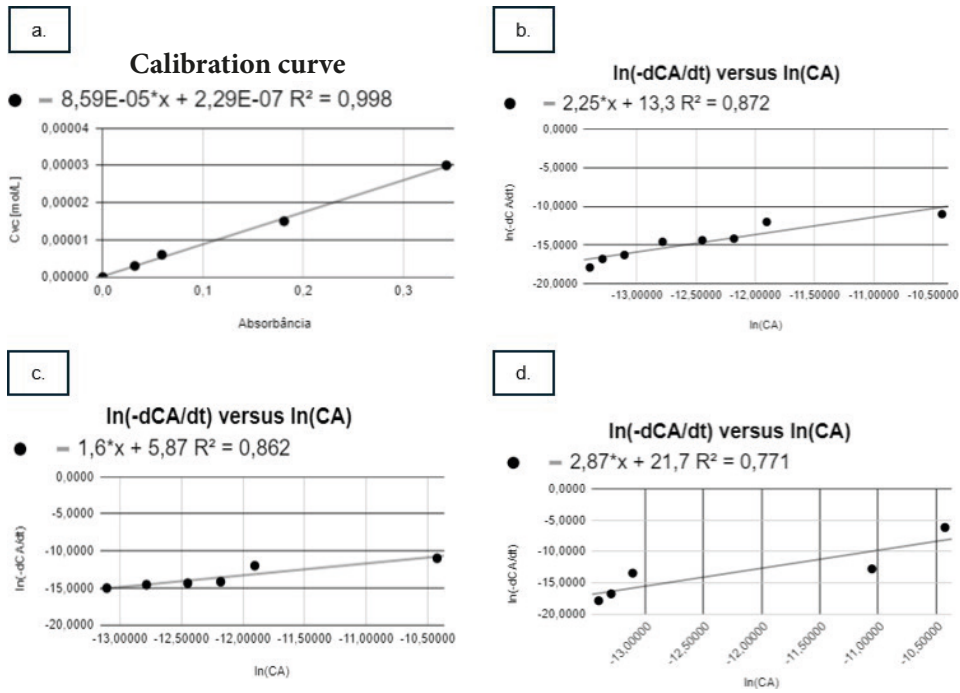


Figure 3 - Results of the calibration curve and application of the method of equally spaced points: 3 - Calibration curve (a); 3 - Method of equally spaced points at all points, considering 10 min as the first point in the interval (b); 3 - Method of equally spaced points up to the time of 10 min, with a step of 2 min (c); 3 - Method of equally spaced points, obtaining the absorbance of the time 5 min by interpolation and with a step of 5 min (d).

Source: From the authors, 2024.

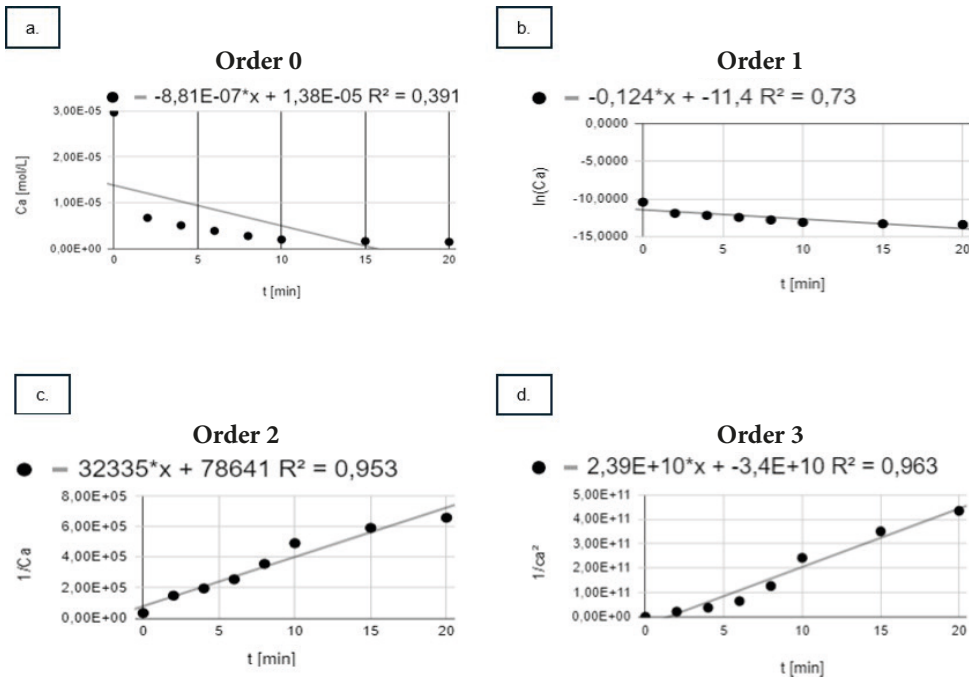


Figure 4 - Application of the integral method: 4 - Integral method assuming order 0 (a); 4 - Integral method assuming order 1 (b); 4 - Integral method assuming order 2 (c); 4 - Integral method assuming order 3 (d).

Source: From the authors, 2024.

MODELING THE CSTR REACTOR

The total mass balance and mass balance equations per component, considering a second order approach, described by Equations 16, 17 and 18, were implemented for the reagents NaOH (C_B) and Crystal Violet (C_A). Using *Scilab* software, the height and volume of the liquid in the reactor and the concentration profiles were simulated, based on the initial conditions obtained in the flow tests.

Figure 5 (yellow line) shows the height of the liquid in the reactor as a function of time, indicating that the height remains constant at approximately 1.4 dm over time. This behavior suggests that the reactor has reached a steady state, where the inlet flow rate is equal to the outlet flow rate, keeping the volume constant.

As can be seen in the graph identified by the blue line, the volume of liquid in the reactor remains constant at approximately 2.5 dm³ over 25 minutes. This result reinforces that the reactor is operating in a permanent regime, where the fluid input rate is equal to the output rate.

The graph labeled with the red line shows a rapid initial decrease in the concentration of Crystal Violet, followed by stabilization. The sharp decrease in concentration in the first few time instances can be attributed to the high reactivity of Crystal Violet with NaOH. The subsequent stabilization suggests that the system has reached a dynamic equilibrium, where the reaction rate is equal to the reagent feed rate.

The final value of C_A obtained was 3×10^{-6} mol/dm³. Similarly, the graph in Figure 5 (green line) shows a rapid decrease in NaOH concentration, followed by stabilization. The stabilization trend is slower compared to Crystal Violet, reflecting the initial conditions of higher concentration of NaOH and the stoichiometry of the reaction. The final concentration of C_B obtained was 0.039 mol/dm³.

FLOW TESTS

Several tests were carried out to determine the flow rate at which each compound would be inserted into the reactor, as well as the CSTR's outlet flow rate. Table 2 shows the tests for the reactor's outlet flow rate; looking at the table, it was concluded that the best flow rate is 0.260, in the ¼ open position. At this flow rate, the CSTR presented a more stable and consistent output. This suggests that the flow condition provided an adequate balance between the input and output, minimizing possible unwanted variations in the process.

valve position identification number	Valve positions	t [min]	m [g]	Volume [L] (m/ρ)	F [L/min]	Average F [L/min]
1	Open	0,32	490,77	0,492	1,554	1,387
		0,38	515,34	0,517	1,348	
		0,38	481,62	0,483	1,260	
2	Open ¼	1,00	58,13	0,058	0,058	0,054
		1,00	52,97	0,053	0,053	
		1,00	50,36	0,050	0,050	
3	Open ½	1,00	272,83	0,274	0,274	0,260
		1,00	262,31	0,263	0,263	
		1,00	243,39	0,244	0,244	

Table 2. CSTR output flow.

Source: Authors, 2024.

In addition to the reactor outlet flow tests, tests were also carried out on the reactor inlet, in the ¼ open, ½ open and fully open positions, as shown in Table 3. Analyzing the table, it can be seen that the average flow values are different due to the sensitivity of the choke; the slightest change in any position can lead to fluctuations in flow.

However, the best flow rates were F_{Ae} , the crystal violet flow rate, at the ¼ aperture, as shown in Table 4, and F_{Be} , which represents the NaOH flow rate, also at the ¼ aperture.

Once the flow tests had been carried out, with a ¼ opening in the chokes of the two equipment pipes, flow rates of 0.084 L/min

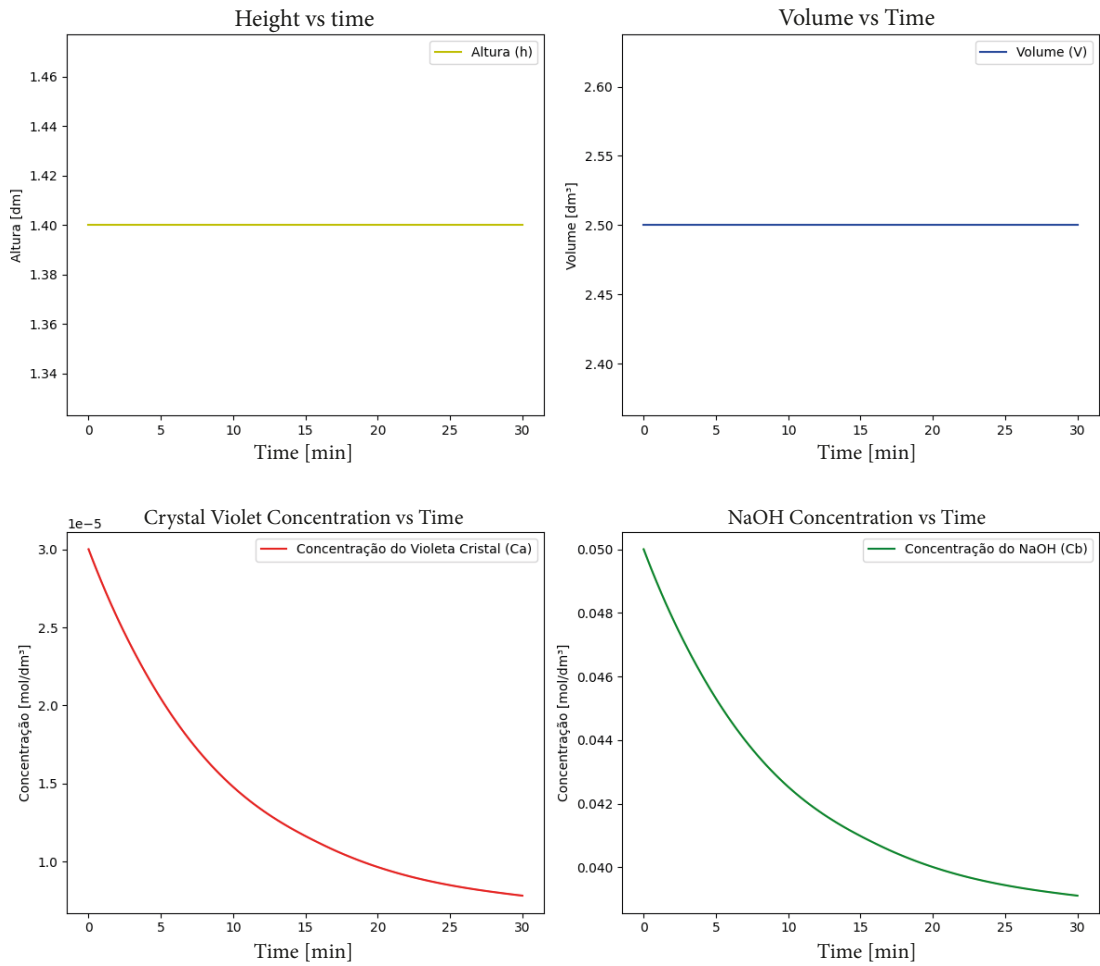


Figure 5 - Graphs of Height (h), Volume (V), Crystal Violet Concentration (C_A) and NaOH Concentration (C_B) over Time.

Source: Authors, 2024.

Valve	Valve positions	t [s]	t [min]	m [g]	Volume [L] (m/ρ)	F [L/min]	Average F [L/min]
FAe	$\frac{3}{4}$ Open	60	1,00	50,72	0,051	0,051	0,084
		60	1,00	126,21	0,127	0,127	
		60	1,00	73,47	0,074	0,074	
FBe	$\frac{3}{4}$ Open	60	1,00	291,93	0,293	0,293	0,285
		60	1,00	285,47	0,286	0,286	
		60	1,00	275,42	0,276	0,276	

Table 4: CSTR inlet flow rate.

Source: Authors, 2024.

Valve	Valve positions	t [min]	m [g]	Volume [L] (m/ρ)	F [L/min]	Average F [L/min]
FAe	Open ½	1,00	68,14	0,068	0,068	0,072
		1,00	58,15	0,058	0,058	
		1,00	88,87	0,089	0,089	
FBe	Open ½	1,00	58,68	0,059	0,059	0,064
		1,00	77,72	0,078	0,078	
		1,00	55,99	0,056	0,056	
Valve	Valve positions	t [min]	m [g]	Volume [L] (m/ρ)	F [L/min]	Average F [L/min]
FAe	Open	1,00	417,88	0,419	0,419	0,340
		1,00	259,69	0,260	0,260	
FBe	Open	1,00	284,78	0,286	0,286	0,334
		1,00	380,71	0,382	0,382	
FBe	¼ Open	1,00	41,35	0,041	0,041	0,040
		1,00	38,22	0,038	0,038	
FBe	¼ Open	1,00	381,56	0,383	0,383	0,397
		1,00	409,61	0,411	0,411	

Table 3. CSTR input flow.

Source: Authors, 2024.

for Crystal Violet and 0.285 L/min for NaOH were obtained, resulting in a CSTR outlet flow rate of 0.369 L/min. It is important to note that the valve at the outlet of the CSTR reactor is a block valve, so its use for regulation is being carried out due to the unavailability of resources. Due to this factor, even when operating the valve in the same position as the three studied, there will be some fluctuations in the value of the outlet flow.

Despite these fluctuations, the potential energy resulting from the liquid column of the two reactant reservoirs is sufficient to keep the inlet flow rates constant, as long as the reservoirs are refilled regularly during the experiment, giving steady-state operation.

EXPERIMENTAL TESTS WITH THE CSTR

To start up the CSTR reactor, a load of 2.5 L of Crystal Violet solution at 3×10^{-5} mol/L was fed. Once the tanks were completely filled, the timer was started and both inlets and outlets were opened. Stirring was maintained at speed 3 during the process. Samples were taken at 2 min intervals until the total operating

time was 10 min; after that, the sampling times continued at 5 min intervals until the final operating time was 25 min. Using the calibration curve, the measured absorbance values were converted to mol/L. It should be noted that, as the NaOH reagent is in excess, the measurements using the spectrophotometer were always taken considering the first value read, as the reaction continues to take place inside the cuvette. The values of time versus concentration are shown in Table 5.

Reactions in the CSTR	
t [min]	CVC [mol/L]
0	3,25E-05
2	2,45E-05
4	1,93E-05
6	1,48E-05
8	1,17E-05
10	9,68E-06
15	7,19E-06
20	6,24E-06
24	5,98E-06
25	5,90E-06

Table 5. Concentrations collected in the reaction operated at the CSTR.

Source: Authors, 2024.

Once the data had been collected, DTR calculations were carried out to obtain the actual residence time and adjustments to confirm the reaction k previously obtained in a batch system. Equations 19, 20, 21 and 22 were used to obtain, respectively, the theoretical residence time of the system, the DTR function, the area under the curve and the error in % in relation to the actual residence time of the system, obtained by the difference between the total area and the area under the DTR curve. The values obtained are shown in Table 6.

The values obtained for theoretical and actual residence time were 6.78 and 5.32 min respectively, resulting in an error of 27.56%, a value considered optimal, which indicates that the system operates close to the flow rate established by the flow tests. In addition, the error value shows that, despite fluctuations in the flow rate of the outlet valve, the reactor is able to operate under conditions close to those stipulated in theory.

DTR	
Total area	25
Area under the curve	19,685
τ Real [min]	5,315
τ Ideal [min]	6,779
Error [%]	27,56
Integral Method	
Order 1	$-0.0646 \cdot x + -10.6 \quad r^2 = 0.895$
Order 2	$5856 \cdot x + 34851 \quad r^2 = 0.971$

Table 6. DTR data and integral methods for obtaining the constant k

Source: Authors, 2024.

With the same time and concentration data collected, it was possible to apply the integral method for orders 1 and 2 to confirm the k obtained in the batch reaction. The fit for order 1, shown in Table 6, generated an excellent r^2 , showing greater reliability in the proposed fit. Thus, the k obtained for pseudo-first order was 0.0646 min^{-1} ; dividing this value by the

concentration of NaOH used in the reaction gave a k value of 1.26 L/mol.min . Hypotheses raised regarding the decrease in the reaction rate constant are the temperature of the reaction medium and the real concentrations of NaOH, which are constantly prepared in large volumes to replenish the reservoirs. Even so, the values obtained in the experimental test are satisfactory, with greater confidence compared to the test carried out in batch operation with the aid of a beaker.

RESIDENCE TIME DISTRIBUTION (RTD) CALCULATIONS AND CONVERSIONS

With the data obtained, it was possible to process it to obtain the 1st and 2nd times of the DTR, for application in the segregation, serial tank and dispersion models. In addition, the real concentrations of the reagents used during the test were used in the balance equations for an ideal CSTR and for a CSTR model with dead zones. Table 7 shows the parameters obtained for each of these models, with the conversion value per final time adopted to represent the real conversion of the system. The volume used for the calculations was the same as that used for the initial load of Crystal Violet, 2.5L.

The conversion adopted as the final for the assembled system, shown in Table 7, resulted in 81.84% for the Crystal Violet reagent, which is the optimum value for the assembled system. Based on this value, the model that comes closest to it should be chosen for future operations. For the ideal models, three variations of the balance were considered, since the flow rate of the Crystal Violet inlet is not the same as the flow rate of the reactor outlet, making it necessary to account for the NaOH inlet flow rate. Model 4, shown in Table 7, which considers an outlet flow rate of 0.369 L/min , provided a conversion similar to that of the general balance (Model 1) and the CSTR model with zones this suggests that the

Models	Parameters	Conversion(x)
DTR treatment	$t_m = 8.619$ min and $\sigma^2 = 52.252$ min	-
Conversion by time	-	0,8184(last point)
Segregation	-	0,5239
Tanks in series	$\tau = t_m$ $n = 1.422$ and $\tau_i = 6.0621$ min	0,9534
	$\tau = \tau_{teo}$ $n = 0.8797$ and $\tau_i = 7.7067$ min	0,8626
	$\tau = \tau_{ideal}$ $n = 0.5406$ and $\tau_i = 9.8309$ min	0,7540
Dispersion	$\sigma^2/tm^2=0.7033$ $Pe_s = 1.1624$ $Da = 0.4380q = 1.5834$	0,3184
Ideal CSTR(4 models)	Model 1: Considering overall balance (Equation 37)	0,2281
	Model 2: Considering <i>Scilab</i> data	0,9015
	Model 3: Conventional design ($F_0 = F_{Ac} = 0.084$ L/min)	0,4933
	Model 4: Conventional design ($F_0 = F = 0.369$ L/min)	0,2476
CSTR with dead zones	$\alpha = 1,17$ $\beta = 0,011$ $F_s = 0.0831$ L/min $\tau = 35.2087$ min $C_{As} = 2.55 \cdot 10^{-5}$ mol/L $C_A = 2.56 \cdot 10^{-5}$ mol/L	0,2130

Table 7. Models used and their respective parameters and conversions obtained

Source: Authors, 2024.

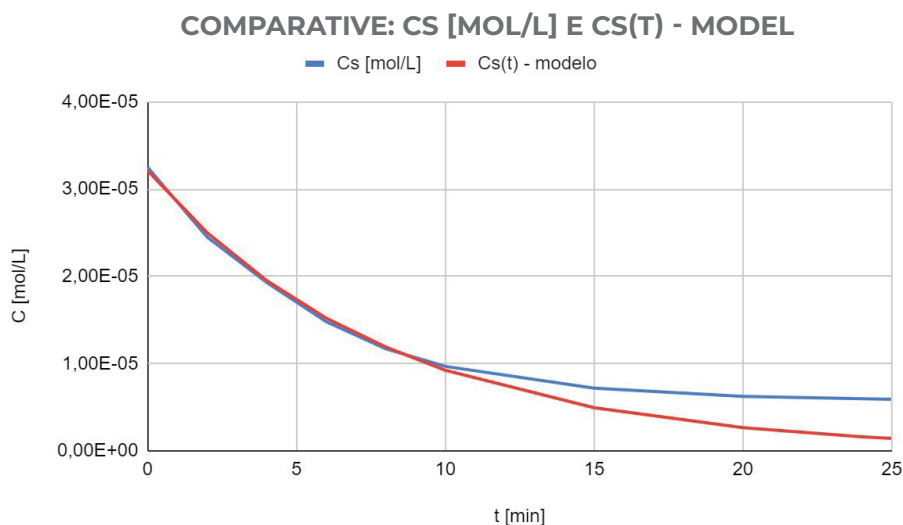


Figure 6. Comparison between experimental data and CSTR model for dead zones

Source: Authors, 2024.

latter may better describe the system in terms of ideal models.

However, this model manages to describe the behavior of the system up to 10 min of operation, as can be seen in Figure 6, which indicates the need to adapt the modeling proposed by Fogler to better describe the reaction system set up.

The conversion obtained from the *Scilab* data points to the decreasing behavior of the two reagents, following the expected trend for conversion, which indicates that, even with

the ideal conditions used for the simulation, the model is able to describe the behavior of the real system assembled by the students well, so minor adjustments to the simplifications used are necessary.

For the other methods, the conversion obtained by the segregation model was higher than that obtained by the ideal models and lower than the actual conversion obtained, representing an error due to the approximation of the liquid flow in globules that behave like batch reactors. The dispersion model, despite

being used more for non-ideal PFR reactors, showed a conversion closer to the ideal and to the CSTR with dead zones, indicating that the axial dispersion hypothesis is able to match the dead zone and preferential channel formation scenarios, although it shows a very low conversion compared to the real one.

Finally, the series tank model shows the best conversions, even for the variations made within the calculations, and is the best empirical model for describing the behavior of the CSTR assembled by the students, resulting in conversions very close to the real one when considering the theoretical and real residence times. This indicates that future efforts to adjust the CSTR's outlet valve, changing the type of valve from blocking to regulating, would be able to reduce the error in relation to residence time, which would consequently result in a better prediction of the system's conversion using the series tank model.

CONCLUSIONS

The results of determining the reaction rate constant and modeling the CSTR reactor provide a detailed view of the kinetics between Crystal Violet and NaOH. The construction of the calibration curve and the use of the integral and equally spaced points methods indicate pseudo-first order kinetics, with significant variations in the rate constant depending on the method applied.

Although the method of equally spaced points has high sensitivity, the fits suggest that

the reaction occurs between orders 1 and 2. On the other hand, the integral method offers a more reliable coefficient of determination (r^2) for the pseudo-first order, with a rate constant of $k' = 0.124 \text{ min}^{-1}$, confirmed later with kinetic data in CSTR, showing $k' = 0.0646 \text{ min}^{-1}$ for pseudo-first order and $k = 1.26 \text{ L/mol.min}$ for second order.

In addition, the flow tests and the analysis of the residence time distribution in the CSTR show performance close to what was expected, even with fluctuations in the flow rate and an error of 27.56% in the residence time. These results indicate that the system is close to the desired steady state.

Modeling with approaches such as segregation, serial tanks and dispersion provide important parameters for analyzing the reactor's performance. These results demonstrate the relevance of modeling and kinetic analysis to optimize the process and ensure its efficiency under real conditions.

Finally, the analysis of the CSTR models, both ideal and non-ideal, highlights the importance of the input flow rate and the characteristics of the system. The model with dead zones proved effective up to 10 minutes, but requires adjustments to predict long-term behavior. The time conversion of 0.8184 confirms the reactor's efficiency, with the series tank model being the most suitable for describing the system after adjustments in residence time.

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