Original Article

DEGRADATION KINETICS OF ORGANIC MATTER IN DAIRY INDUSTRY WASTEWATER BY FLOTATION/OZONATION PROCESSES

CINÉTICA DE DEGRADAÇÃO DA MATÉRIA ORGÂNICA NAS ÁGUAS RESIDUÁRIAS DA INDÚSTRIA DE LATICÍNIOS PELOS PROCESSOS DE FLOTAÇÃO/OZONIZAÇÃO

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ABSTRACT: This study evaluated the adjustment of four kinetic models and their respective parameters on data of dairy wastewater treatment by the physico-chemical process of flotation and ozonation. The experiment was implemented during the year 2014, with all the tests in triplicate. The treatments were carried out at different pH levels (3.6, 7.0 and 10.4), and flotation/ozonation was catalyzed by manganese (Mn^{2+}) in neutral level (pH 7.0). Best removal efficiencies for chemical oxygen demand (COD) were obtained in acidic medium, with removals greater than 75% after 20 min of treatment. There was no significant difference with regards to addition of Mn^{2+} on COD removal by the physico-chemical process. The kinetic models that best fit to the experimental data, for all treatments, were the asymptotic (residual) model and that of Chan and Chu. Treatment in acidic medium showed the highest values of the kinetic parameters for the adjusted model, obtaining a k coefficient equal to 0.2394 min^{-1} for the asymptotic model and kinetic coefficient $1/\rho$ of 0.4816 min^{-1} for the Chan and Chu model, both presenting a determination coefficient greater than 99%.

KEYWORDS: Asymptotic model. Chan and Chu model. AOP.

INTRODUCTION

Wastewater from the dairy industry contains high concentrations of nutrients and organic matter when compared to domestic wastewater (PRAZERES et al., 2012). To minimize the impacts of the treated dairy effluents not meeting the discharge standards on water bodies, new technologies are required. In recent decades, Advanced Oxidation Processes (AOPs) have been used as an alternative for the treatment of wastewaters from various processes (TRIPATHI et al., 2011; AVSAR et al., 2012; WU et al., 2012).

In the case of the dairy industry, there has been an intensified use of flotation in recent years, either by dispersed or dissolved air (CARVALHO et al., 2018). Flotation is a process of wide application in the treatment of oily wastewater, as an alternative preliminary treatment in the dairy industry for the removal of fat from industrial wastewater, which can harm the functioning of the treatment system (METCALF; EDDY, 2015).

There are already some published reports on flotation using ozone instead of atmospheric air to enhance the efficiency of the treatment systems (LEE et al., 2008; KIM et al., 2011).

Ozone can act as an AOP able to react with various organic compounds due to its high oxidation potential. AOPs are chemical treatment processes in which reactive species such as the hydroxyl radical (•OH) are generated and capable of oxidizing most organic compounds present in wastewater.

According to Gottschalk et al. (2000), for ozonation in acidic medium (pH < 4), the direct reaction mechanism predominates, i.e., via molecular O_3. As the pH increases, a larger quantity of •OH radicals are formed. For pH values exceeding 10, the decomposition of O_3 into •OH radicals is instantaneous and the indirect reaction mechanism predominates (via •OH radicals). At pH levels around 7 the two reactions may occur, both direct and indirect, due to the presence of oxidizing agents.

Most of the compounds present in wastewaters react directly with ozone in reactions with extremely high rate constants, which indicates its use in reducing or eliminating these undesirable compounds (BELTRÁN, 2004). The understanding of the reactions rates occurring in wastewater treatment plants is important for design and operation of the reactors (SPERLING, 2014).

The formation or disappearance of compounds present in wastewater is described as the reaction rate r, and the relationship between the rate of reaction, reagent concentration and reaction order. According to Sperling (2014), in wastewater

treatment systems the most frequent reactions are of order 0 and 1.

There are studies reporting that the first order kinetic model efficiently describes the removal of different compounds present in industrial wastewater by the ozonation process (GIRI et al., 2010; HASSANI et al., 2013). Chan and Chu (2003) proposed a non-linear pseudo first-order kinetic model to describe the degradation of pesticides in water by Fenton reagent. The regression results indicated that the degradation kinetics were well described by the proposed model.

Thus, the objective of this study was to fit first-order kinetic mathematical models and estimate their respective kinetic parameters to describe the degradation of organic matter in synthetic dairy wastewater by flotation/ozonation.

MATERIAL AND METHODS

The experiment was made during the year of 2014 using a synthetic wastewater to simulate the dairy industry wastewater, obtained by the addition of whole milk to distilled water to get a COD concentration of approximately 2,000 mg L^{-1} (BRIÃO; TAVARES, 2007).

After preparation of the synthetic solution the alkalinity of the sample was measured, finding an average value of 75.56 mg L^{-1} $CaCO_3$. This analysis is important to account for the presence of carbonates that may interfere with the treatment.

Ozone gas was obtained from an ozone generator Model O&L 10.0 RM, developed by the company Ozone & Life® (São Paulo, Brazil). The method used to quantify the ozone gas concentration was iodometry, by indirect titration (APHA, 2012).

Treatment by flotation/ozonation was performed in a washing flask (Pyrex) with 1 L capacity, where near its base was a porous diffuser (pores with 40~60 µm aperture) through which ozone gas with the concentration of 42 mg L^{-1} was introduced at a flow of 1.0 L min^{-1}. Table 1 shows the conditions to which samples of the synthetic dairy wastewater were submitted for the tests.

Table 1. Conditions of the synthetic dairy wastewater used to obtain the degradation kinetics of organic material

Test	$[O_3]$ (mg L^{-1})	$[Mn^{2+}]$ (mg L^{-1})	pH
1	42.0	-	3.6
2	42.0	-	7.0
3	42.0	-	10.4
4	42.0	0.04	7.0

Batch tests were performed for an O_3 exposure period of 240 min. During the reaction, samples were taken at times of 0, 10, 20, 40, 60, 90, 120, 180 and 240 min. Each test was carried out in triplicates and the COD removal was analyzed using the colorimetric method (APHA, 2012).

To explain the degradation of organic material present in the synthetic dairy wastewater four first-order kinetic models or their modifications were tested as presented in Equations 1 to 4. The equations represent the kinetic models of plug flow, continuous stirred tank reactor, residual model and Chan and Chu's model, respectively.

$$\frac{C}{C_0} = e^{(-kt_h)} \quad (1)$$

$$\frac{C}{C_0} = \frac{1}{1+kt_h} \quad (2)$$

$$\frac{C}{C_0} = (1 - C^*)\, e^{-kt_h} + C^* \quad (3)$$

$$\frac{C}{C_0} = 1 - \frac{t_h}{\rho + \sigma t_h} \quad (4)$$

For fitting of the kinetic models average experimental data was not used, but instead the data of the three samples were used. If the average was adopted there would be an increase in the R^2 value. For measure the fittings, values of square root of the mean square error (RMSE), adjusted coefficient of determination ($R^2_{adjusted}$) and R^2 were used.

The kinetic models studied were fitted to the observed data with the aid of the software Origin 9.1 (Origin Lab Corporation, Northampton, MA, USA). Determination of the kinetic coefficients was performed by nonlinear regression using the Levenbert Maquart algorithm.

RESULTS AND DISCUSSION

Figure 1 shows the average values with their respective standard deviations, for COD removal along the reaction period for the test conditions.
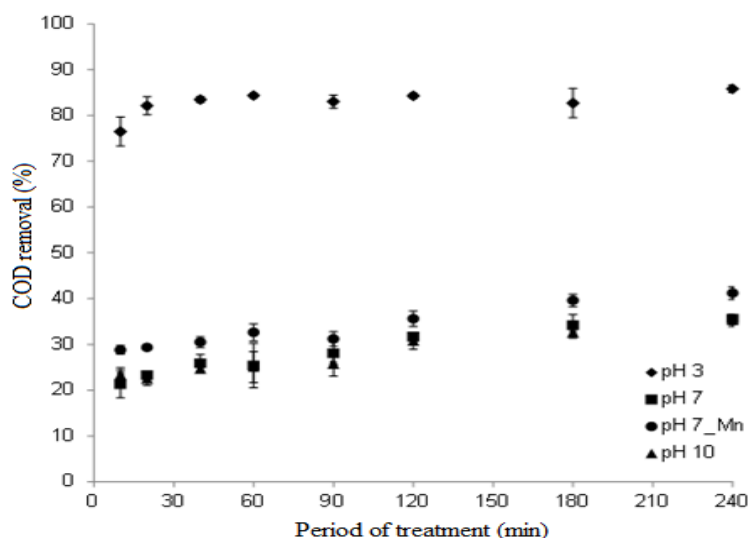
Figure 1. Effect of pH on COD removal from the synthetic dairy wastewater using flotation/ozonation process (42 mg L^{-1} of ozone)

From Figure 1 it was observed that the acidic wastewater (pH 3.6) showed better removal of COD with efficiency values greater than 75% in the first 10 min of treatment. On the other hand, removal efficiencies were very low for pH 7 and 10.4. One explanation for this reduced efficiency of ozonation at pH 10.4 and 7.0 compared with pH 3.6 may be due to the presence of bicarbonates and carbonates in milk, and therefore in the wastewater ($[CaCO_3]$ = 75.56 mg L^{-1}). The presence of "sequestrants" of hydroxyl radicals such as carbonates, bicarbonates and humic substances may reduce the efficiency of oxidation processes performed by this oxidizing agent (•OH), as in ozonation at high pH levels (LEGRINI et al., 1993; MASTEN; DAVIES, 1994).

Another explanation for the higher COD removal in acid medium is due to the natural coagulation/flocculation of milk proteins in the dairy effluents. According to Quick (1974), casein is the major protein found in milk (about 80%) and has an average isoelectric point at pH 4.6, therefore at this pH casein is found at its point of lowest solubility due to the decrease of intermolecular repulsions.

Without coagulation, both air bubbles and particles carry negative zeta potentials, negative charges. When particles approach, air bubbles the electrical double layers surrounding the particles and bubbles overlap causing a repulsive force, so that bubble collision and attachment is poor. For good coagulation, chemistry conditions and higher flotation efficiencies, it is expected that the flocs formed have little or no electrical charge, so electrostatic forces are low or near zero (EDZWALD, 2010).

Thus, part of the organic load may be removed by flotation (particles present in suspension adhere to ozone gas bubbles generated in the absorber bottle) and this aggregate (bubble - particle) has a lower density than the suspension, thus it will rise in the aqueous solution and can be physically removed.

The wastewater under basic conditions (pH=10.4) submitted to ozonation showed better results than the neutral (pH=7) wastewater. However, during the 240 min of ozonation COD removal did not exceed 42%. Addition of the catalyst (Mn^{2+}) showed no significant effect on the removal of COD from the wastewater.

Some authors (ASSALIN et al., 2006; MAHMOUD; FREIRE, 2007) observed improved removal efficiency of the organic load from wastewater when the catalyst Mn^{2+} was added to the ozonation process, at concentrations exceeding 1 mg L^{-1}. Therefore, the non-significance of Mn^{2+} addition may be explained by the low concentrations ($[Mn^{2+}]$ < 0.04 mg L^{-1}) used in this study.

Fitting of the models based on first order kinetics to the experiment data was obtained using the software SigmaPlot 12.0 (Systat Software Inc., San Jose, CA, USA) and the coefficients for each model are presented in Table 2.

Table 2. Fits of the 1st order COD removal models to the results obtained for each test.

Model	Parameter	pH 3.6	pH 7	pH 7/ Mn^{2+}	pH 10.4
1	k (min^{-1})	0.1267	0.0028	0.0027	0.0035
	R^2	0.7162	0.3794	0.4952	0.6839
	$R^2_{adjusted}$	0.7162	-0.3794	-0.4952	-0.6839
	RMSE	0.5382	0.3828	0.3791	0.5904
2	k (min^{-1})	0.2162	0.0038	0.0036	0.0051
	R^2	0.8616	0.0901	0.2156	0.3004
	$R^2_{adjusted}$	0.8616	-0.0901	-0.2156	-0.3004
	RMSE	0.2624	0.3025	0.3082	0.4559
3	k (min^{-1})	0.2394	0.0933	0.1272	0.1487
	C*	0.1639	0.6975	0.7130	0.6521
	R^2	0.9939	0.8553	0.8256	0.8916
	$R^2_{adjusted}$	0.9938	0.8495	0.8256	0.8873
	RMSE	0.0114	0.0401	0.0425	0.0380
4	$1/\rho$	0.4816	0.0413	0.0529	0.0859
	$1/\sigma$	0.8625	0.3325	0.3121	0.3714
	R^2	0.9893	0.9282	0.8819	0.9094
	$R^2_{adjusted}$	0.9889	0.9254	0.8819	0.9058
	RMSE	0.0202	0.0251	0.0288	0.0251

First order kinetic models: (1) Plug flow PFR; (2) Continuous stirred tank CSTR; (3) Asymptotic or Residual; (4) Chan and Chu.

It can be observed (Table 2), that for all treatments the highest R^2 and $R^2_{adjusted}$ values found were obtained for the models Asymptotic and Chan and Chu. These models also had the lowest estimated error values (RMSE).

Salgado et al. (2009) also used the kinetic model of Chan and Chu to obtain the efficiency of the photolytic AOP for removal of color in synthetic wastewater containing Indigo Carmine. For the model parameters, these authors found values for ρ^{-1} and σ^{-1} of 0.65 and 1.06, respectively, very close to those found in the present study when using pH 3.6.

In Chan and Chu model, the inverse of the constant ρ corresponds to an initial COD degradation rate, consequently the higher the ρ^{-1} faster is the removal of COD from the wastewater. Moreover, the inverse of σ corresponds to the maximum possible conversion or maximum degradation of COD.

Figures 2 and 3 shows the regression curves for the dairy wastewater at pH(s) 3.6, 7, 10.4 and pH 7 with and without the presence of Mn^{2+} using the asymptotic (or residual) model and the Chan and Chu model respectively.

From Figures 2 and 3 it can be seen that the results of COD removal at the pH(s) 10.4, 7 and 7 with the manganese catalyst were very similar. There was no significant difference (95% confidence interval) between the regression models of pH 7 and 7/Mn (CARVALHO; CHRISTOFFOLETI, 2007). Therefore, this further confirms that the addition of 0.04 mg L^{-1} of the catalyst did not enhance the flotation/ozonation efficiency

According to Figures 2 and 3, from a kinetic point of view it can be observed that the experiment in acidic medium (pH 3.6) was most efficient, presenting the most promising kinetic constants, k equal to 0.2394 min^{-1} for the asymptotic or residual model and ρ equal to 0.4816 min^{-1} for the model of Chan and Chu .

Santos et al. (2011), while treating wastewater containing the azodye Red GRLX-220 to ozonation, also found that the kinetic constant of the pseudo-first order model was higher in acidic medium ($k = 0.174$ min^{-1}) compared to the basic medium ($k = 0.154$ min^{-1}). However, Mahmoud and Freire (2007) studied the kinetic behavior of ozonation for the degradation of the azodye Remazol Black B, and found that the kinetic constant in basic medium was higher ($k = 0.035$ min^{-1}) when compared with the kinetic constant obtained in acid medium (0.0067 min^{-1}).

Kern et al. (2012) studied conventional ozonation of wastewater from a hospital laundry. The authors found that in acid medium (pH 3 to 3.5) the kinetic constant of COD degradation was 0.0036 min^{-1}, with a coefficient of determination equal to 97%.

Analysis of the confidence intervals (95%) shows a significant difference for ozonation in neutral and basic media, where treatment at pH 10.4 gave better results with respect to the neutral medium.
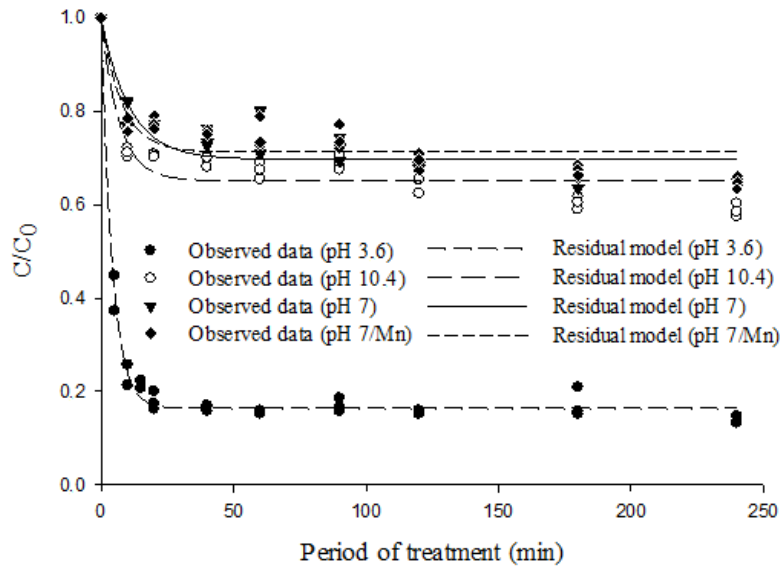
Figure 2. Asymptotic or residual model fitted to the observed data for flotation/ozonation at pH 3.6, 7, 10.4, and 7 with or without presence of the Mn^{2+} catalyst
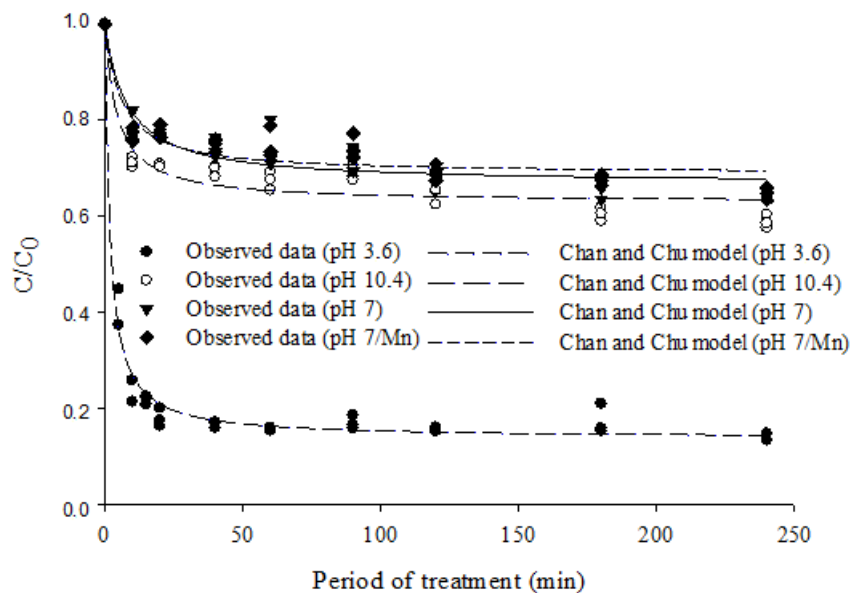

Figure 3. Chan and Chu model fitted to the observed data for flotation/ozonation at pH 3.6, 7, 10.4, and 7 with or without presence of the Mn^{2+} catalyst

Table 3 shows the equations obtained for the asymptotic and Chan and Chu kinetic models, as well as the respective required periods of flotation/ozonation calculated to remove 75% of COD from the synthetic dairy wastewater. The value of 75% was adopted based on the DN COPAM/CERH-MG 1/2008, which established that the minimum limit for wastewater discharging into a receiving water body, with respect to COD is 180 mg L^{-1}, i.e., the treatment must be 75% efficient, with no alteration to the original conditions of the water body.

The asymptotic or residual model considers that a recalcitrant fraction (C_r) of the organic compound is not degraded. Therefore, based on the obtained coefficients (C^*), for the acidic medium the remaining COD concentration would be 328.0 mg L^{-1}, while for the neutral pH this concentration could be 1427.0 mg L^{-1}.

Table 3. Adjusted kinetic equations, their respective coefficients and the period of treatment necessary to remove 75% of the COD

Model	Equation	$t_{75\%}$ (min)
Residual	$\dfrac{C}{C_0} = (1 - 0.1639)\, e^{-0.2394 t_h} + 0.1639$	9.51
Chan and Chu	$\dfrac{C}{C_0} = 1 - \dfrac{t_h}{2.0764 + 1.1594 t_h}$	11.94

Because the asymptotic and Chan and Chu models showed good fit to the COD degradation kinetics, considering the synthetic dairy wastewater ozonized in acidic medium (pH 3.6) at an ozone concentration of 42 mg L^{-1}, the treatment period required to satisfy legislation may vary between 9.51 and 11.94 min for the wastewater to reach discharge standards, with respect to COD.

CONCLUSIONS

The degradation of organic matter in synthetic dairy wastewater by flotation/ozonation was investigated. For all treatments the kinetic models that best fitted to the experimental data were the asymptotic or residual model and the model of Chan and Chu.

Ozonation in acidic medium (pH 3.6) was the treatment that presented the highest kinetic constants for the adjusted models. For the asymptotic model a kinetic constant (k) of 0.2394 min^{-1} was obtained, and for the model of Chan and Chu the kinetic constant ($1/\rho$) was found to be 0.4816 min^{-1}. For both models the coefficient of determination (R^2) was greater than 0.99.

RESUMO: Neste estudo, avaliou-se o ajuste de quatro modelos cinéticos (modelo de escoamento pistonado, mistura completa, assintótico ou residual e de Chan e Chu e seus respectivos parâmetros, na degradação da matéria orgânica presente no efluente de laticínios pelo processo físico-químico de flotação e ozonização. O experimento foi implementado durante o ano de 2014, com todos os testes em triplicata, os s tratamentos foram realizados sob diferentes pHs (3,6; 7,0 e 10,4), além da flotação/ozonização catalisada pelo manganês (Mn^{2+}) em meio neutro. Observando que em meio ácido ocorreram as melhores eficiências de remoção da demanda química de oxigênio (DQO), tendo sido obtida uma remoção superior a 75% em 20 min de tratamento. Não houve diferença significativa em relação à adição de Mn^{2+} ao processo físico-químico. Os modelos que mais se ajustaram aos dados experimentais, para todos os tratamentos realizados, foram o modelo assintótico e o de Chan e Chu. O tratamento em meio ácido foi o que apresentou os maiores valores dos parâmetros cinéticos para os modelos ajustados, obtendo-se para o modelo assintótico, coeficiente k igual a 0,2394 min^{-1}, e para o modelo de Chan e Chu, coeficiente cinético $1/\rho$ de 0,4816 min^{-1}, apresentando para ambos os modelos um coeficiente de determinação superior a 99%.

PALAVRAS-CHAVE: Modelo assintótico. Modelo de Chan e Chu. POA

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