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Sequential coagulation treatment and processes based on ozone (O_3, O_3/UV, O_3/UV/H_2O_2) for remediation of agro-food industrial wastewater

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ABSTRACT

Cassava wastewater is a liquid resulting from the processing of cassava in the production of flour and extraction and purification of starch. Conventional treatment processes are inefficient for this kind of effluent; therefore the objective of this study was to evaluate coagulation followed by O_3, O_3/UV, and O_3/UV/H_2O_2 reactions for degradation of cassava wastewater. Coagulation achieved reductions of about 70% in COD (chemical oxygen demand), which increases the practicability of sequential use of ozonation and its combinations. The use of ozone reduced the absorbance of samples at 393 nm in the course of processes, and among the evaluated systems, combination O_3/UV/H_2O_2 was the most favorable in reducing effluent absorbance (74%), besides providing the highest kinetic degradation constant ($2,236 \times 10^{-3}$ min^{-1}). The turbidity and COD were reduced by 95% and 30%, respectively, after combined coagulation and ozonation processes. Toxicity tests indicated the structural modification of organic components of cassava wastewater, due to lower effluent toxicity after evaluated treatments. Thus, the potential of ozone-based reactions for degradation of organic matter, especially of the compounds that provide color and turbidity to the effluent, was verified through evaluation of absorption spectra and their kinetics.

Keywords: Advanced oxidation processes; Cassava wastewater; Ozonation; Tertiary treatment; Wastewater reclamation

1. Introduction

Cassava (*Manihot esculenta* Crantz) is the most important tuberous root in tropical and subtropical regions of the world, being the third source of carbohydrates (behind only rice and corn) [1]. According to the Food and Agriculture Organization of the United Nations (FAO), world production of cassava remains at an accelerated rate of growth, averaging 281 million tonnes per year [2]. Cassava can be found *in natura* and also processed as flour and starch, contributing to the food supply for more than 700 million people [3]. Processing of cassava leads to cassava wastewater generation that is a light-yellow milky-colored liquid effluent resulting from the pressing the grated mass of cassava roots used for flour production and starch extraction and purification processes [4]. It is a residue rich in starches, proteins, salts, several substances, and linamarin, a cyanogenic glycoside, released after cellular disruption of the

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root structure under enzymatic hydrolysis. Since linamarin is soluble in water, this compound is almost completely eliminated with washing water from cassava processing [4]. Consequently, the release of this waste can lead to a reduction of dissolved oxygen, eutrophication and reduction of the auto depuration capacity of water bodies, and death of aquatic fauna and animals that consume water with an excess of cyanide gas [5,6]. For each ton of processed cassava, an average volume of 0.25 m^3 of cassava wastewater is generated [7]. In addition to being of great contribution in the industry, they contain a high organic load, attributed to high concentrations of carbohydrates (starch, cellulose, hemicellulose) [8], conferring significant environmental pollution when untreated in water bodies [9], having a population equivalent of 200 people/d [4].

Most of the cassava processing industries do not have adequate management for cassava wastewater. Because of this, studies that seek their valorization and/or treatment process can be found in the literature. Some examples are the use of biological treatment of effluents, both aerobic and anaerobic (activated sludge, stabilization ponds, biodigesters) [5]; fertirrigation; insect, fungus, and parasite control [10]; and biosurfactants and substrate for microorganisms in production of molecules of interest [11,12]. Although several references to cassava reject and effluent treatment are available, the final destination of cassava wastewater is still uncertain. There are reports of low efficiency in color removal [13], high energy spent and excessive biomass production in aerobic systems [14], low nutrient removal efficiency such as nitrogen [15] and phosphorus, and long hydraulic retention times in anaerobiosis and space required for installation of ponds/filters [16]. When used in fertirrigation, soil and plant damage may occur, and there is a risk of leaching of potassium ion (found in high concentration in the tailings) by rainwater and irrigation, which can contaminate both surface and underground water bodies [17]. Another aggravating factor is that not all companies are close to the field receiving fertigation and/or biopesticide application, implementation costs are very high, or the practice is prohibited in the release of environmental licenses for new projects. Thus, cassava wastewater is often considered an environmental liability.

Combination of conventional processes and advanced oxidation processes (AOPs) show a possible alternative for the treatment of real effluents, in accordance with various papers available on the subject [18–27]. AOPs are characterized by generation of hydroxyl radical (·OH), with a potential reduction of 2.8 V, in which oxidation reactions occur rapidly, not-selectively and efficiently, at atmospheric temperature and pressure and can even mineralize complex organic molecules [28–30]. Therefore, AOPs have been used because they are considered clean technologies (by destruction of pollutants with complete mineralization) that increase biodegradability and reduce toxicity of wastewater when applied as pre or post treatment, able to degrade dissolved organic compounds and even emerging pollutants that could not be destroyed by conventional treatment [31,32].

Oxidation techniques include Fenton, Photo-Fenton, ozonation and peroxidation reactions combined or not with UV radiation, and photolysis with UV radiation [33]. In particular, ozonation includes, among other advantages, color removal, reduction of suspended solids, turbidity, COD (chemical oxygen demand) and TOC (total organic carbon) of waters and effluents [19]. Also, gaseous ozone can be applied directly to the sample, which does not increase effluent and sludge volume, and only a short time is required for the reaction [34].

Advanced oxidation of organic pollutants involves a sequence of complex reactions [35,36]. Thus, it is common to apply mathematical models to describe the kinetics of effluent treatment via AOPs mainly in real industrial waste, in an attempt to better describe reaction pathways of the complex molecule mixtures contained in them [37]. Another important parameter for predicting AOPs is acute toxicity assessments. Since several contaminants resist these processes and their degradation can occur incompletely, there is a possibility of formation of smaller intermediates that are as toxic as the original pollutants [32]. Literature on the subject suggest that *Artemia salina* is a representative bioindicator in the surveys, since it is capable of reporting toxicity in synthetic and real effluents from a wide variety of sources [38–40], assessing the effectiveness of water and wastewater treatment and the degree of environmental safety [41].

Thus, we aimed to evaluate the coagulation/flocculation process followed by the ozonation process for cassava wastewater treatment. Different systems of AOPs were used with the use of O_3 (O_3, O_3/UV, O_3/UV/H_2O_2), aiming at absorbance, turbidity, COD, TOC, phosphorus, total, volatile and fixed solids reduction of the effluent. With spectral scan data, it was possible to perform an analysis of a kinetic model, since this information is related to the organic load, color, and turbidity of the real effluent studied, accompanying decay of this parameter for a proposal of remediation of cassava wastewater. Also, another purpose of the research was to verify acute toxicity after treatment with ozonation, using the microcrustacean *Artemia salina* as test organisms.

2. Materials and methods

2.1. Cassava wastewater and characterization

The research was carried out using real effluent obtained after the pressing stage of cassava in a starch production unit in the north central region of Paraná, Brazil. Wastewater was stored under refrigeration at 4°C. For purposes of sample characterization, we determined: pH (pHmeter Tecnopon model mPA210, Piracicaba, Brazil), turbidity (turbidimeter Del Lab model DLT-WV, Araraquara, Brazil), electrical conductivity (Digimed model DM-3 conductivity meter, São Paulo, Brazil), COD (closed reflux as described in APHA [42]), TOC (Shimadzu carbon analyzer model TOC 5000-A, Kyoto, Japan), total, volatiles, fixed solids (gravimetry as described in A.O.A.C. [43]) and sedimentable solids (Imhoff cone method according to NBR 10561 [44]), volatile acidity, alkalinity and total phosphorus [42]. Due to the suspended solids content and a high organic load of the material, coagulation pretreatment prior to ozonation processes was performed.

2.2. Coagulation/Flocculation

In order to adapt the best conditions in COD removal for primary treatment of cassava wastewater, an experimental design 3^2 was carried out, with four replications at the central point, varying the pH and concentration of coagulant agent solution ($FeCl_3$) (Sigma-Aldrich/Vetec, Rio de Janeiro, Brazil) for coagulation, as in Table 1.

Working pH of 5.0 and 6.0 were chosen because both are near values to the real effluent pH and neutral pH 7.0 where it is possible that the competition of ozone action mechanisms occurs. Coagulant agent concentrations of 800, 1000, and 1200 mg L^{-1} were chosen based on the studies of Suarez et al. [45] in treatment of real effluent.

Coagulation/flocculation processes was conducted with 250 mL of raw effluent, 10% (v/v) coagulant solution and 2% (v/v) cationic acrylamide polymer (flocculating agent). Samples were shaken for 20 min [10 min of rapid stirring (100 rpm) on the addition of a coagulant and 10 min of slow stirring (50 rpm) on flocculant addition], after coagulation and subsequent sample filtration. We determined COD at each point in the planning, in triplicate. From a multiple comparison test for this analysis (Tukey's test, $\alpha = 0.05$, using the software Statistica - Stat Soft® version 10), a pH and $FeCl_3$ concentration conditions were chosen to be applied as a pre-treatment to the tertiary effluent.

Spectral scans (800–200 nm) of coagulated cassava wastewater were performed as a preliminary test at different pH conditions [adjusted with 1 mol L^{-1} sodium hydroxide solution (NaOH)] to verify absorption peaks and follow reactions of AOPs at these wavelengths.

2.3. Ozonation

Ozonation reactions and ozone-based AOPs were conducted by batching in a jacketed glass reactor of 90 mm in diameter, 200 mm in height, and 1000 mL in volume at a controlled temperature using a thermostatic bath (Visomes Plus model V550, São Paulo, Brazil, at 25 ± 1ºC) as shown in Fig. 1.

Table 1
Experimental planning used in coagulation experiments

Experiments	pH	$[FeCl_3]$ (mg L^{-1})
1	6.0 (0)	1200 (+1)
2	7.0 (+1)	1000 (0)
3	5.0 (-1)	800 (–1)
4	5.0 (–1)	1000 (0)
5	7.0 (+1)	1200 (+1)
6	6.0 (0)	800 (–1)
7	7.0 (+1)	800 (–1)
8	5.0 (–1)	1200 (+1)
9	6.0 (0)	1000 (0)
10	6.0 (0)	1000 (0)
11	6.0 (0)	1000 (0)
12	6.0 (0)	1000 (0)

Note: pH adjustment was performed by adding drops of 10% NaOH solution.

Ozone was generated from atmospheric oxygen by an ozone generator (Philozon O_3R model ID-10, Balneário Camboriú, Brazil), in a 50% (V/V) O_2/O_3 mixture. The ozone input flowrate was fixed to all assays (1.5 g O_3 $h^{-1)}$ and was used as the inlet ozone gas concentration (25 mg O_3 L^{-1}) according to the calibration curve provided by the manufacturer. The ozone consumed in relation to ozone inlet was between 30% and 35% in accordance with Guzmán et al. [46]. Treatments were performed with O_3 injection, O_3/UV, and O_3/UV/H_2O_2 combinations (H_2O_2 concentration of 100, 500, and 1000 mg L^{-1} - Sigma-Aldrich/Vetec, Rio de Janeiro, Brazil) with 200 mL of wastewater in each experiment. Chosen H_2O_2 concentrations were based on studies by Rodríguez-Chueca et al. [24], Riaño et al. [47] and Cao and Mehvar [48]. Radiation was generated by a filament of a mercury vapor lamp, inserted in center of the reactor using a protective bulb of quartz (UV-C radiation, $\lambda = 254$ nm). After the start of each reaction, every 5 min, aliquots of 1 ml were withdrawn in the initial 30 min of the process and in 10 final min for UV-Vis spectrophotometric analysis (800–200 nm) to observe spectral variations of samples. At the end of processes, we determined pH, turbidity, COD, TOC, total, volatile and fixed solids for the effluent.

2.4. Kinetic model

For application of a kinetic model for the purpose of analyzing effluent concentrations derived from processing of cassava, P_m, the following homogeneous reaction was considered:

$$P_m + O_3 \rightarrow C_m \quad (1)$$

where P_m is the initial effluent and C_m is the treated effluent. According to Fogler [49], the rate of reaction is considered as:

$$-P_m = k_m C_m^{\alpha} C_{O_3}^{\beta} \quad (2)$$

where k_m is the reaction rate constant, C_m is cassava wastewater concentration, C_{o_3} is ozone concentration, α is the order the of reaction, and β is the order of reaction of ozone.

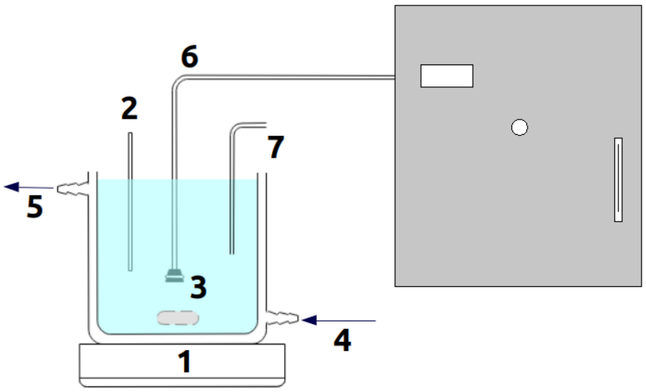

Fig. 1. Representation of experimental unit of ozonation. 1: Magnetic stirrer; 2: Sample collector; 3: O_3 disperser; 4 and 5: Inlet and outlet thermostatic bath water; 6: O_3 gas inlet; 7: Residual O_3 outlet.

In this way, the kinetic model proposed here considers the batch process. Consequently, the mass balance equation is given as:

$$A = E - S + G - C \tag{3}$$

where A is the accumulated mass effluent rate, E is the rate of effluent entering the reactor, S is the mass flow rate of effluent leaving the reactor, G is the mass effluent rate that is generated in reactor, and C is the rate of mass of effluent that is consumed in the reactor. When considering the batch process, $E = 0$, $S = 0$, in other words, no component enters or leaves the reactor. It is also considered that no other components are generated inside the reactor. Thus, the rate of change of mass consumed of effluent (C_p) in relation to time is equal to P_m; therefore, C_p can be described by:

$$\frac{dC_p}{dt} = -k_m C_m^{\alpha} C_{O_3}^{\beta} \tag{4}$$

Considering that ozone flow rate is high enough, that there is saturation inside the reactor, i.e. $C_{O_3}^{\beta} = k_0$ (k_0 is the concentration of ozone, constant in system). And also considering that the sample effluent concentration is proportional to the absorbance at a suitable wavelength, i.e., $C_p = k_a A_\lambda$ ($A\lambda$ is being absorbance at the evaluated wavelength). Thus, the first order ordinary differential equation is obtained (Eq. 5).

$$\frac{dA_\lambda}{dt} = -k_m k_0 k_\alpha^{\alpha-1} A_\lambda^{\alpha} \tag{5}$$

Therefore, the solution of Eq. (5) in the intervals of $A_0 - A_1$ and in the period of time $t_0 - t_1$, is given by Eq. (6).

$$A(t) = \left(A_0^{1-\alpha} - k_m k_0 k_\alpha^{\alpha-1}(1-\alpha)(t-t_0)\right)^{\frac{1}{1-\alpha}} \tag{6}$$

where $A(t)$ is absorbance at a given time (t) and A_0 is initial absorbance.

Since k_m and k_0 are constants, they can be considered as a single coefficient $k' = C_a e^{\frac{-E_a}{RT}}$ (Arrhenius equation), where k' is the reaction rate constant, C_a = Arrhenius constant, E_a = activation energy, R = is the gas constant (8.314 J K^{-1} mol^{-1}), and T = temperature in Kelvin. Thus, it is possible to generalize Eq. 6 in the form:

$$A(t) = \left[A_0^{1-\alpha} - C_a e^{\frac{-E_a}{RT}} k_\alpha^{\alpha-1}(1-\alpha)(t-t_0)\right]^{\frac{1}{1-\alpha}} \tag{7}$$

with Eq. (5) and the least squares method, absorbance spectra are adjusted to obtain parameters E_a, C_a, α, and k.

2.5. Ecotoxicological tests

Acute toxicity of untreated effluent and tertiary post-treatment was evaluated in *Artemia salina* (brine shrimp) following the method described by Meyer et al. [50] with some adaptations. Saline solution (30 g L^{-1} of sea salt in distilled water) was used as a means for cyst hatching and maintenance of individuals. Test organisms of 48 hours of life were exposed to samples in concentrations of 100, 50, 25, 10, and 1% (v/v) and controls (saline and sodium dodecyl sulfate - SDS, Panreac Química, Spain) over 48 h at 27–30°C. After 24 and 48 h, the number of immobile organisms was counted, a characteristic that shows toxicity to nauplii. Data were analyzed by the Probit method (using Statistica - Stat Soft®, version 10 software), with the objective of estimating effective concentration to 50% of nauplii with 95% of reliability. Samples with EC_{50} less than 1000 ppm (1000 mg L^{-1}) were considered toxic [50].

3. Results and discussions

3.1. Primary treatment: coagulation

Table 2 describes characteristics of raw cassava wastewater.

Comparatively, the chemical composition of this effluent is variable, being influenced by factors such as plant variety, environmental conditions of cultivation, processing to obtain cassava flour, and processes used to treat effluent [55]. Cassava wastewater is a residue that contains high organic load, attributed to the presence of high concentrations of carbohydrates (starch, cellulose, hemicellulose), proteins, salts, and other substances [8], which increases its content of organic matter (content found in fractions of volatile solids and measured indirectly by COD). Agro-industrial effluents are characterized by their great environmental impact when not treated and in general, do not contain recalcitrant substances [56]. However, cassava wastewater presents low pH, high COD, TOC, and suspended solids [3], evidenced by our analytical response obtained that confirmed their dangerousness.

Primary treatment prior to oxidation processes is a fundamental step for reduction of COD of cassava wastewater since one of the main limitations of AOP is the range in which major degradations are reached, in concentrations

Table 2
Physical-chemical characteristics of cassava wastewater

Parameter	Raw effluent	Literature*
pH	3.74 ± 0.02	5.50
Turbidity (NTU)	171 ± 2	3910
COD (mgO_2 L^{-1})	16884 ± 1239	60000–100000
TOC (mg L^{-1})	2892.4 ± 6.24	2604
Total solids (%)	0.912 ± 0.091	0.23–0.66
Volatile solids (%)	0.247 ± 0.117	0.06–0.2
Fixed solids (%)	0.665 ± 0.133	0.16
Sedimentable solids (mL L^{-1})	69 ± 4	15
Conductivity (µS cm^{-1} 20°C)	1792 ± 1	961
Alkalinity (mg$CaCO_3$ L^{-1})	4102 ± 466	889
Volatile acidity (mgCH_3COOH L^{-1})	17500 ± 1136	5366
Total phosphorus (mg L^{-1})	3484 ± 87	83.3
Fe_{total} (mg L^{-1})	17.4 ± 0.4	8

*References: Campos et al. [5]; Colin et al. [51]; Damasceno et al. [52]; Ferraz et al. [53]; Magalhães et al. [55]; Ribas and Barana [54]; Sun et al. [3].

lower than 5000 mg L^{-1} [47,57]. The pH values were select to become favorable primary and tertiary treatments. The compound $FeCl_3$ is a coagulating agent that acts in a wide range of pH, being observed to aid the formation of good flakes in pH of 4.0 to 11.0 [58]. As for ozone, it is recognized that its action on the degradation of organic matter can occur in two ways: direct attack, favored at acidic pH, and indirect in which several oxidation mechanisms coexist, resulting from initiation reactions of radicals generated by self-decomposition of ozone [59]. In this way, the chosen working range was pH 5.0, 6.0 (both pHs close to the actual effluent), and 7.0 (neutral pH, where it is possible that the competition of ozone action mechanisms occurs).

Ferric chloride is the most used coagulant in the treatment of industrial effluents, and it is of fundamental importance to evaluate pH parameters and salt dosage to improve process efficiency and reduce operating costs [60]. Coagulant agent concentrations of 800, 1000 and 1200 mg L^{-1} were chosen based on the studies of Suarez et al. [45] who studied the treatment of real effluent (hospital wastewater) with COD in the range of 375–2464 mg O_2 L^{-1} in concentrations of 0–200 ppm of $FeCl_3$. Knowing initial COD of cassava wastewater, concentrations of $FeCl_3$ were six times higher with proportions of salt found in literature.

Fig. 2 presents mean COD reduction of samples (difference between COD of raw effluent and COD after primary treatment) in coagulation/flocculation assays at proposed pH and $FeCl_3$ concentration conditions.

We observed that higher COD reductions were statistically different ($p < 0.05$) between $FeCl_3$ treatments (concentration of 1200 mg L^{-1}) at pH 5.0 and 6.0. For sequential treatment of ozonation, conditions of experiment 1 (pH = 6.0, 1200 mg L^{-1} $FeCl_3$) were chosen since the decomposition of ozone is favored at near alkaline pH [61], and there was no statistical difference ($p > 0.05$) between COD removal averages at pH 5.0 and 6.0 (11600 and 11689 mgO_2 $L^{-1)}$. Moreover, literature data indicate that effluents with high concentrations of bicarbonate ions (represented by alkalinity data) tend to be strong inhibitors of indirect reactions between hydroxyl radicals and organic matter. Since inorganic carbon acts as a hydroxyl radical scavenger, the reaction rate of organic compounds with radicals is insignificant, and direct oxidation with organic substrates becomes predominant [47]. Therefore, when treating cassava wastewater, it is interesting to favor reactions with ozone via a direct mechanism.

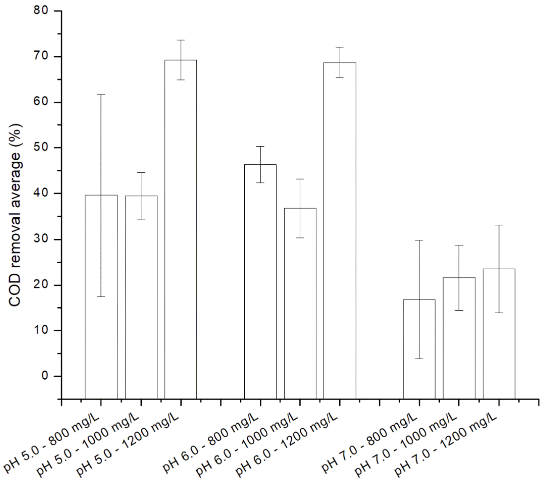

Fig. 2. Percentage of COD removal as a function of pH at different concentrations of $FeCl_3$ in cassava wastewater coagulation.

In Fig. 3, the percentage reduction in turbidity, COD, phosphorus, and total solids of effluent treated by coagulation/flocculation at pH 6.0 and a concentration of 1200 mg L^{-1} of $FeCl_3$ is observed.

It is possible to affirm that primary treatment contributed to the decay of fundamental parameters for control of cassava wastewater treatment, making sequential process of ozonization and its combinations possible.

3.2 Tertiary treatment and ozonation kinetics

Fig. 4 shows UV-Vis spectral scans of cassava wastewater at different pH conditions. With increasing pH, the

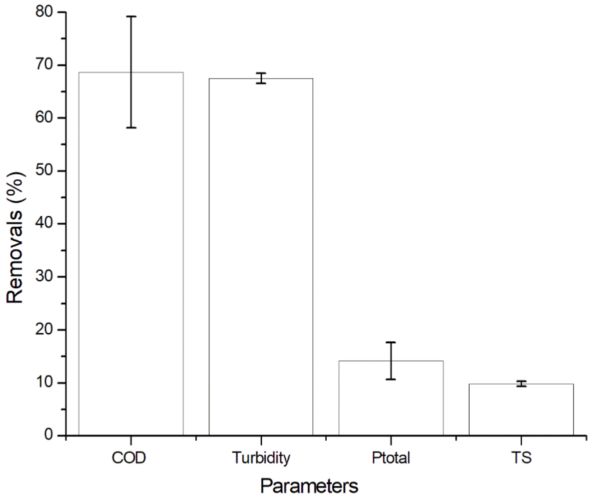

Fig. 3. Percentage removals of COD, turbidity, phosphorus (Ptotal), and total solids (TS) values in cassava wastewater after coagulation/flocculation.

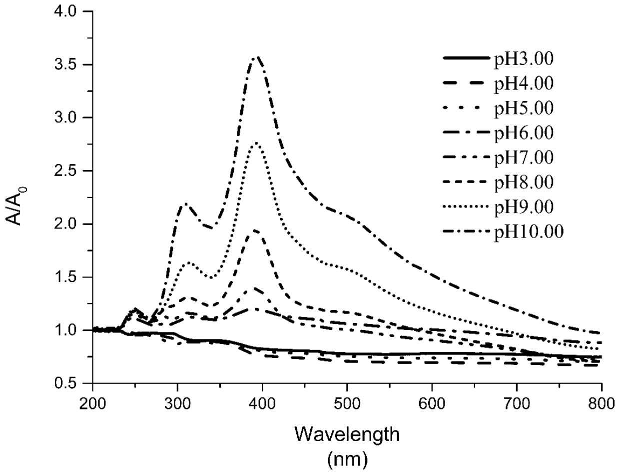

Fig. 4. Variation of absorption spectra (800–200 nm) of cassava wastewater at pH 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, and 10.0.

absorption band becomes more evident. Because it is a real sample of complex composition, it does not have characteristic peaks described in the literature, hence the importance of this evaluation.

To adjust the proposed kinetic model, we used a wavelength absorbance of 393 nm; the peak was identified by spectral scans between 800–200 nm. Determination of kinetic constants in effluent treatment processes is an important tool to describe and predict system performance [3]. In this case, application of a model to follow decay of absorbance of samples submitted to ozonization was proposed due to simplicity in evaluation technique and the linear relationship between absorbance and concentration of effluent (Beer's law), as well as being associated with turbidity data and color. The choice of H_2O_2 concentrations was based on studies by Rodríguez-Chueca et al. [24], Riaño et al. [47] and Cao and Mehvar [48], in which satisfactory analytical responses were obtained, mainly regarding removal of the organic load in the treatment of strong effluents from food processing via AOPs.

Adjustment parameters of the kinetic model [Eq. (7)] for treated samples by ozone, O_3/UV, and O_3/UV/H_2O_2 are described in Table 3.

Fig. 5 shows the fit of the model to experimental data of evaluated processes.

It was possible to verify that in processes with O_3, O_3/UV and O_3/UV/H_2O_2 (at 100, 500, and 1000 mg L^{-1} of H_2O_2) there was an accelerated removal of organic matter due to the sharp decay of absorbance between 5 and 25 min, followed by a slower degradation stage between 30 and 40 min, justifying the ozonation process of no more than 40 min of reaction.

The rate kinetic constant (k) in the O_3/UV/H_2O_2 system was twice as high as treatment with exclusive use of O_3. Higher rate constants are expected in ozone-based effluent treatment processes [62–64]. Bigger rate kinect constants were found using peroxide 500 and 1000 mg $L^{-1.}$

Reductions in absorbance values were more significant in the combined process O_3/UV/H_2O_2. For tests using 500 and 1000 mg L^{-1} of H_2O_2, we observed cassava wastewater coloration was altered and improved within the first 10 min, being the most representative period in ozonation combined to UV and H_2O_2 of effluent, indicating the potentiality of these advanced processes for degradation of color. These results indicate that at the start of the reaction, readily oxidizable compounds are cleaved, and in the course of the oxidation process, these compounds become less available and some generated intermediates become hydroxyl radical scavengers, competing radicals with undegraded molecules [46]. Therefore, ozone alone did not present satisfactory results, since absorbance remained close to 1.0, even after 40 min of reaction. With the O_3/UV system, lower absorbances were obtained after 40 min of reaction, a rather prolonged time compared to the combined treatments with lower and shorter ozonation times.

Data in the literature indicate that in initial stages of ozonation at acidified pH, direct molecular ozone reaction pathways are carried out, and it reacts with double bonds and functional groups of organic compounds present in effluent, causing incomplete oxidation and with the generation of intermediates resistant to oxidation chain reactions [19,46]. At this stage, therefore, high color removal - indicated by the absorbance data - as well as the formation of molecules that maintain effluent resistant to removal of COD and TOC can be observed in data from treated effluent (Table 4).

Another important point is the role of UV and H_2O_2 alone and their combined effect. In this study, these systems were not used by reports in the current literature of low efficiency of these processes in the treatment of effluents. Ultra-

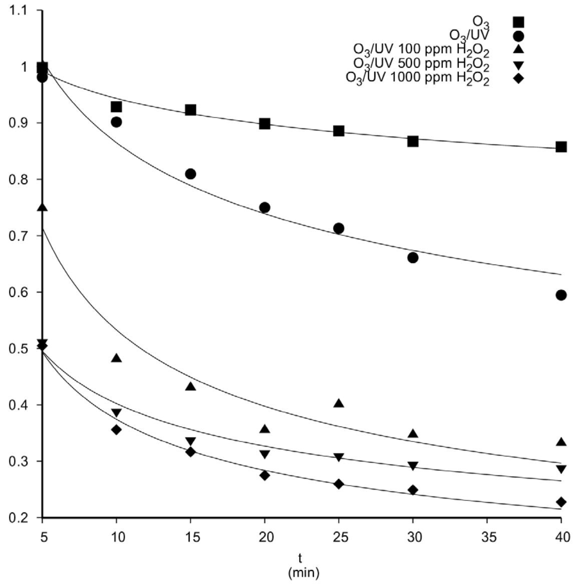

Fig. 5. Evolution of absorbance decay at 393 nm experimental as a function of reaction time in different ozonation systems (O_3, O_3/UV, O_3/UV /H_2O_2 in 100, 500, and 1000 mg L^{-1}). Experimental points (symbols), model fitted to experimental data (lines).

Table 3
Parameters of fit of the kinetic model of studied samples

	O_3	O_3/UV	O_3/UV 100 mg L^{-1} H_2O_2	O_3/UV 500 mg L^{-1} H_2O_2	O_3/UV 1000 mg L^{-1} H_2O_2
α	1.0013	1.0356	1.0021	1.0634	1.0200
E_a (J mol^{-1})	4585.35	56414.8	2106.75	4437.9	1090.82
k (s^{-1})	1.104×10^{-3}	1.507×10^{-3}	1.513×10^{-3}	2.235×10^{-3}	2.236×10^{-3}
C_a (s^{-1})	50.0882	35.1671	50.8341	52.2168	50.1466
R^2	0.9798	0.9796	0.9896	0.9293	0.9631

violet photolysis is usually used for disinfection purposes and is dependent on the ability of the compounds to absorb the emitted light [65]. The efficiency of direct photolysis is enhanced when irradiation is combined with hydrogen peroxide, whose photo catalytic dissociation provides enough energy to break the O-O bounds and yields ·OH radicals, thus facilitating the degradation processes of different compounds. Hydrogen peroxide has a relatively high oxidant potential ($E^{0\ 1.77\ V}$), but alone does not lead to the generation of hydroxyl radicals. The slow reaction rates make the process ineffective when oxidizing more refractory and recalcitrant pollutants. Moreover, H_2O_2 is only considered an AOP when combined with another agent, like UV [66].

As a result of studied treatments, absorbance at 393 nm presented representative decays, especially in the O_3/UV/H_2O_2 system, which also showed significant reductions in turbidity. The proposed model has a minimization of errors for an estimation of absorbances that eventually are proportional to the concentration of organic matter, color, and turbidity. Such an estimate and error minimization is given by Pearson coefficient (R^2), which shows the quality of adjustments, reaching R^2 between 0.93 and 0.99.

Results of Eq. 7 are in agreement with those found in Table 4, because after treatment by ozonation and its combinations, we observed the decay of physical-chemical parameters of real effluent. Table 4 shows averages of turbidity, COD, TOC, total (TS), volatile (VS), and fixed solids (FS) in pretreated effluent and after the ozonation processes.

In turbidity, all treatments differed significantly; the highest reduction (95%) was obtained in O_3/UV/H_2O_2 1000 mg L^{-1} process. In COD, there was no statistical difference in different treatments applied, but reductions in organic matter higher than 30% were observed. For TOC, combination O_3/UV/H_2O_2 with peroxide concentrations of 500 and 100 mg L^{-1} did not differ between concentrations of H_2O_2, and other samples had significant differences in reduction of this parameter. However, low removals of TOC were observed in all treatments. The addition of peroxide and UV, in general, improves the results of AOPs, due to photolysis of ozone, better mass transfer and greater generation of hydroxyl radicals [63]. However, a dose of peroxide must be carefully adjusted, because concentrations above optimal values make H_2O_2 a radical scavenger [46,67]. In the present study, we found that concentrations of 500 and 100 mg L^{-1} of H_2O_2 were insufficient to achieve higher efficiencies regarding degradation, indicating that concentrations ≥ 1000 mg L^{-1} peroxide have great potential for effluent decomposition. About of total, volatile and fixed solids, better results were obtained with O_3, with a maximum reduction of 12%. The pH in the ozonation experiments, even in the systems combined with UV and H_2O_2, remained very close to the initial value, on average 5.11 ± 0.37.

Fig. 6 shows the qualitative results of sequential treatment of cassava wastewater by coagulation followed by ozonation (O_3/UV/H_2O_2 1000 mg L^{-1} system).

3.3. Acute toxicity: *artemia salina*

Toxicity tests are fundamental in assessing effects on an environmental scale when considering the release of industrial effluents. Because it is not possible to detect all substances individually contained in this complex mixture,

Table 4
Mean* of characterization of pretreated effluent (after coagulation step) and treated with O_3, O_3/UV, O_3/UV/H_2O_2 100, 500, and 1000 mg L^{-1}

	Turbidity (NTU)	COD (mg L^{-1})	TOC (mg L^{-1})	TS (%)	VS (%)	FS (%)
Pretreated effluent	55.6 ± 0.6	11953 ± 94	3181 ± 8	0.826 ± 0.004	0.678 ± 0.006	0.147 ± 0.010
O_3	44.7^a ± 0.5	7107^a ± 706	2880^c ± 30	0.734^b ± 0.006	0.597^b ± 0.017	0.137^c ± 0.011
O_3/UV	9.3^c ± 0.3	7642^a ± 139	3141^b ± 24	0.811^a ± 0.021	0.668^a ± 0.020	0.143^c ± 0.001
O_3/UV/H_2O_2 1000 mg L^{-1}	2.7^e ± 0.2	737^a ± 234	3001^d ± 20	0.861^c ± 0.015	0.571^b ± 0.007	0.289^a ± 0.007
O_3/UV/H_2O_2 500 mg L^{-1}	6.4^d ± 0.3	7309^a ± 214	2986^d ± 36	0.877^c	$0.622^{a.b}$	0.254^b
O_3/UV/H_2O_2 100 mg L^{-1}	15.7^b ± 0.3	7053^a ± 47	3441^a ± 37	0.892^c ± 0.005	$0.621^{a.b}$ ± 0.014	$0.271^{a.b}$ ± 0.009

* Averages followed by the same letter in the column do not differ by Tukey test at 5%.

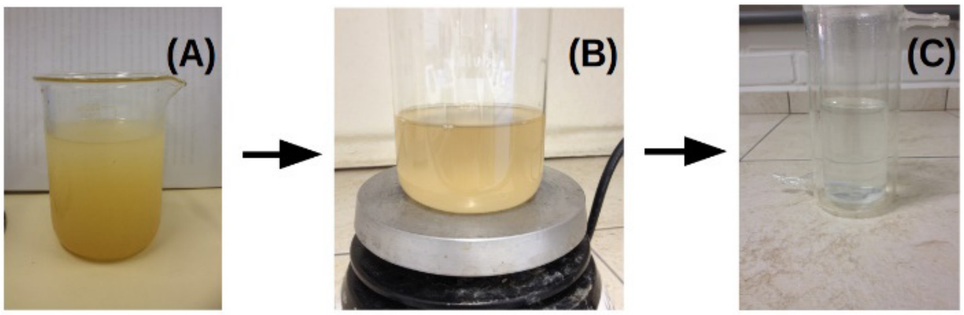

Fig. 6. Appearance of the studied wastewater: (A) Raw wastewater (B) Effluent after coagulation step (C) Effluent after coagulation + O_3/UV/H_2O_2 1000 mg L^{-1}.

controlled and standardized conditions of assays help in comparison of the sensitivity of different organisms to different molecules before and after their treatment [68]. In this study, Artemia salina was chosen as a test organism because of low execution cost of the test, quickly obtained results, and method simplicity when compared to other ecotoxicological evaluations [40].

Fig. 7 shows the percentage of immobility of microcrustacean Artemia salina in untreated cassava wastewater, treated by coagulation, followed by ozonation and its combinations, after 24 and 48 h of incubation, in a concentration of 100% effluent.

We observed that the raw effluent shows a greater response on the immobility of micro crustaceans after 24 and 48 h. After sequential coagulation processes, O_3/UV, and O_3/UV/H_2O_2, the percentage of immobility decreased according to the application of treatments, with the exception of the exclusive use of ozone, which obtained greater immobility of individuals when compared to other treated effluents. The EC_{50} at 24 h SDS positive control was 22.58 μg mL^{-1}. Although considered above the admissible limit, mortality of negative control was less than 4% after 24 h of incubation, which allowed validation of the test [18]. Results of the bioassay (analyzed by the Probit method) indicated an increase in effective concentration (concentration of sample that causes an acute effect – in this case, immobility – to 50% of organisms at time of exposure and test conditions) of cassava wastewater post-treated by ozonation after 24 h of incubation (Table 5). Samples treated by coagulation and coagulation followed by O_3/UV and O_3/UV/H_2O_2 in three concentrations of peroxide showed low toxicity to micro crustaceans at 24 h and 48 h (EC_{50} > 1000 μg mL^{-1}, which does not allow the establishment of the range of EC_{50} in these cases), being considered toxic samples with EC_{50} < 500 μg mL^{-1} [69].

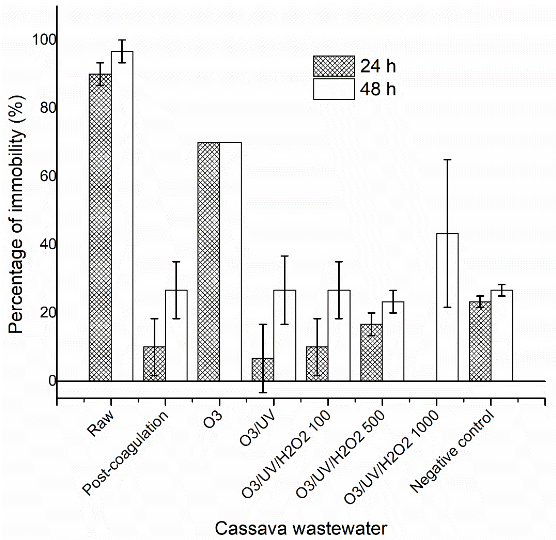

Fig. 7. Percentage of immobility of Artemia salina in cassava wastewater without treatment, post-coagulation, tertiary post-treatments (O_3, O_3/UV, O_3/UV/H_2O_2), and negative control.

These results, according to the literature [69], allow the assumption that in 24 h cassava wastewater, treated or not, presents low toxicity to Artemia salina, since higher EC_{50} after ozonation indicates a reduction in the hazardousness nature of effluent after treatment. Within 48 h, effluent presented moderate and high toxicity pre- and post-treatment, respectively. Thus, aggravation of toxicity was observed throughout the test. It has been shown that, in some cases, a longer exposure period of micro crustaceans provides migration between classifications, sometimes in a representative way. A sample considered to be non-toxic in a period of increased exposure may present significant levels of toxicity, which would not be observed in one test stage. In general, longer exposure time (both of sample in AOPs and potential toxic assessment), higher inhibitions are seen in test organisms [31].

Studies in literature reinforce that *Artemia salina* is a representative bioindicator in research, since it is able to indicate toxicity in synthetic and real effluents from the most diverse sources [20,38–41]. They are useful to identify the presence of metabolites formed during advanced oxidation processes, and they complement traditional physico chemical methods of monitoring effluent treatment. With results of acute toxicity in *Artemia salina*, it can be stated that, for this test organism, combined coagulation to AOPs based on ozone and which combines O_3/UV and O_3/UV/H_2O_2 has ecotoxicological viability as a step in the cassava wastewater treatment process.

4. Conclusion

Complex real effluents, like cassava wastewater, demand a sequence of processes of treatment, whose parameters of operation must be investigated in their diverse combinations, aiming at greater efficiencies. In view of the use of direct oxidation mechanism of organic molecules by ozone action, as well as a higher COD reduction yield (reaching about 68%), pH 6.0 and a coagulant agent concentration of 1200 mg L^{-1} were used in the coagulation step. After reduction of COD, ozonation was applied, and from the modeling of absorbance decay kinetics at 393 nm, promising effects were observed in the O_3/UV/H_2O_2 system with 1000 mg L^{-1} peroxide dosing. In addition to the lower absorbance and turbidity reached, we observed a low toxicity of effluent, as evidenced by reduction of the percentage of immobility in the test organism Artemia salina. With respect to TOC, TS, VS, and FS, treatment with O_3 resulted in higher percentages of reduction. It is recognized that ozonation does

Table 5
EC50 (in μg mL^{-1}) of untreated and ozonated effluent in 24 and 48 h incubation of Artemia salina

EC50 (confidence interval 95%)	Raw effluent		Final effluent	
	24 h	48 h	24 h	48 h
	573.78 (539.26 – 608.30)	102.38 (74.44 – 130.34)	685.87 (638.41 – 733.34)	28.59 (15.31 – 41.86)

not achieve satisfactory efficiencies regarding organic load removal and mineralization of organic compounds; on the other hand, it presents good results in the treatment of water and effluents in terms of turbidity and color, effects that we observed in this study.

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