Kinetic study of ozonation of molasses fermentation wastewater

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Abstract

A kinetic study of molasses wastewater ozonation was carried out in a stirred tank reactor to obtain the rate constants for the decolorization reaction and the regime through which ozone is absorbed. First, fundamental mass transfer parameters such as ozone solubility, volumetric mass transfer coefficients and ozone decomposition kinetics were determined from semi-batch experiments in organic-free solutions with an ionic composition similar that of industrial wastewater. The influence of operating variables such as the stirring rate and gas flow rate on the kinetic and mass transfer parameters was also studied. The application of film theory allows to establish that the reactions between ozone and colored compounds in wastewater take place in the fast and pseudo-first-order regime, within the liquid film. The decolorization rate constants were evaluated at pH 8.7 and 25 °C, varying from 0.6×10^7 to 3.8×10^7 L mol^{-1} s^{-1}, depending on the stirring rate and the inlet gas flow.
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1. Introduction

Environmental problems in beet molasses fermentation factories are mainly related with the production of large quantities of highly loaded and brown colored effluents known as vinasse. Final products of Maillard reaction, mainly melanoidins, are part of vinasse composition. Melanoidins are brown nitrogenous polymers with a largely unknown structure, mainly built up from sugar degradation products [1]. These colorants are formed in the early stages of the Maillard reaction, polymerized through aldol-type condensation and linked by amino compounds, such as amino acids. The complexity of the organic/inorganic matrix of the wastewater and the refractory character of melanoidins make difficult the development of effective treatment schemes for removing colorants. Vinasse is usually subjected to an anaerobic digestion for removing organic matter and producing biogas. After the anaerobic digestion, an aerobic treatment is added to meet discharge norms. However, these treatments are not able to degrade colorants in molasses wastewaters. The discharge of colored effluents into waterways is detrimental to aquatic quality due to the reduction in the photosynthetic activity. Since environmental problems are one of the most important concerning society, especially the wastes produced by industrial activities, it is necessary to develop effective treatment schemes for removing recalcitrant colorants.

Chemical oxidation with ozone presents desirable properties for wastewater treatment because of its high oxidizing character. Ozone is very reactive towards compounds incorporating conjugated double bonds, often associated with color. Ozone can react with solutes either by direct oxidation between organic contaminants and molecular ozone or by indirect reactions with hydroxyl radicals resulting from ozone decomposition. Previous studies [2,3] have shown that ozone is able to react with melanoidins in molasses effluents, reducing color effectively. Despite being a promising technology, there are few studies concerning the ozonation of Maillard reaction products in effluents from molasses-based industries [4]. Moreover, there are no references relating to the ozonation kinetics of melanoidins in molasses effluents. Decolorization of wastewaters by chemical oxidation with ozone is carried out in gas–liquid reactors. Ozone in gas phase is transferred to the liquid phase, reacting with colored pollutants dissolved in water. The global rate depends on the ozone absorption in water and the chemical reaction rate with the dissolved pollutant. So, it is necessary to study every one of these stages individually for a sounded design of wastewater treatment systems.

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Nomenclature

a_v	interfacial area per liquid volume ($m^2\,m^{-3}$)
C_M	molar concentration of melanoidins in wastewater ($mol\,L^{-1}$)
C_{O_3}	molar concentration of ozone in the liquid phase ($mol\,L^{-1}$)
$C_{O_3,SS}$	steady state molar concentration of ozone in the liquid phase ($mol\,L^{-1}$)
$C_{O_3}^*$	equilibrium molar concentration of ozone in the liquid phase ($mol\,L^{-1}$)
D_M	diffusivity of coloring organic matter ($m^2\,s^{-1}$)
D_{O_3}	diffusivity of ozone ($m^2\,s^{-1}$)
E	reaction factor
E_i	instantaneous reaction factor
F_{in}, F_{out}	molar flow rates of ozone at the reactor inlet and outlet ($mol\,s^{-1}$)
Ha	Hatta number
H_{O_3}	Henry's law constant ($kPa\,mol^{-1}\,m^3$)
k_d	ozone decomposition rate constant (s^{-1})
k_L	individual mass transfer coefficient in the liquid phase ($m\,s^{-1}$)
$k_L a_v$	volumetric mass transfer coefficient in the liquid phase (s^{-1})
k_r	decolorization reaction constant ($L\,mol^{-1}\,s^{-1}$)
m	kinetic order of the ozone decomposition reaction
r_d	rate of ozone decomposition reaction ($mol\,L^{-1}\,s^{-1}$)
V	reaction volume (L)
z	stoichiometric factor for the decolorization reaction ($mol\,mol^{-1}$)

Greek letter

ε	extinction coefficient ($L\,mmol^{-1}\,cm^{-1}$)

The aim of this work was to determine the reaction parameters corresponding to the reaction between ozone and melanoidins in molasses fermentation effluents. The kinetic study of ozonation in such heterogeneous system first requires the determination of mass transfer parameters, such as ozone solubility, ozone decomposition rates and the volumetric mass transfer coefficient of ozone in the liquid phase. Once these features are known, the application of film theory can enable the determination of kinetic parameters, such as the stoichiometric coefficient, the ozonation rate constant and the regime of ozone absorption. The effect of operating variables such as the inlet gas flow rate and the stirring rate on physico-chemical parameters was also studied.

2. Materials and methods

Ozonation experiments were carried out in a 2 L jacketed stirred reactor connected to an ozone generator (Sander 301) producing ozone from dry air by electrical discharge. Ozone was fed through a PVDF gas diffuser (Ø12.7 mm × 50 mm, pore diameter 25 µm). All experiments were conducted in semi-batch

mode by sparging the ozone-containing gas continuously into 1 L solution. Temperature was 25 °C and pH was 8.7, the natural of wastewater. Ozone was fed at a mass flow of 1.7 g O_3 h^{-1}. The influence of stirring rate (100, 200 and 400 rpm) and the inlet gas flow rate (100 and 200 L h^{-1}) in reaction parameters was studied.

Mass transfer parameters were determined by monitoring ozone concentration as a function of time into isothermal organic-free aqueous solutions. Aqueous solutions were prepared adding the amounts of salts needed to obtain an ionic strength similar to that of industrial wastewater: alkalinity 8500 mg L^{-1} as $CaCO_3$; sulfate 700 mg L^{-1}; chloride 800 mg L^{-1}; pH 8.7. Samples (30 mL) were taken out periodically to measure pH and dissolved ozone concentration. Ozone analyses were performed using indigo method [5]. Ozone was fed until steady state was reached (ozone concentration in the liquid phase was constant). In that moment, the gas-ozone stream was stopped. The ozone decomposition chemical reaction was then followed determining the concentration of dissolved ozone using the method above mentioned. Experimental runs were conducted in triplicate.

Kinetic parameters were determined from wastewater ozonation experiments. Wastewater was taken from an alcoholic fermentation factory based in beet molasses. After being subjected to an anaerobic/aerobic biological treatment, the wastewater shows the following characteristics: color 2.4 ± 0.1 absorbance units (a.u.) measured at 475 nm; pH 8.7 ± 0.1; COD 3700 ± 100 mg L^{-1}; alkalinity 9000 ± 200 mg L^{-1} as $CaCO_3$; sulfate 700 ± 80 mg L^{-1}; chloride 800 ± 50 mg L^{-1}; ammonium 1000 ± 30 mg L^{-1}; conductivity 22.2 ± 0.6 mS cm^{-1}. Ozone was fed during 40 min. Ozone concentration in the liquid phase was measured using an electrochemical sensor based on the Clark cell method. Samples were periodically withdrawn to analyze color and pH. A description of the analytical methods can be found elsewhere [2].

3. Results and discussion

3.1. Mass transfer parameters

A series of experimental runs of ozone absorption/decomposition were conducted in order to determine mass transfer parameters, such as ozone decomposition rate, the volumetric mass transfer coefficient and ozone solubility. Ozone was bubbled in aqueous solutions with an ionic content similar than that of wastewater in the absence of ozone-reactive compounds [6–8]. The influence of the stirring rate and the inlet gas flow rate on mass transfer parameters was studied. Fig. 1 shows the evolution of dissolved ozone concentration in the experimental runs conducted with organic-free solutions. It should be noted that the initial pH of the solution remained constant throughout ozonation. From Fig. 1a, it can be seen that dissolved ozone concentration in steady state slightly increased from 0.94 to 0.98 mg O_3 L^{-1} when stirring rate was increased from 100 to 200 rpm. A further increase from 200 to 400 rpm did not produce an increase in the steady state ozone concentration. It can also be observed from Fig. 1b that the
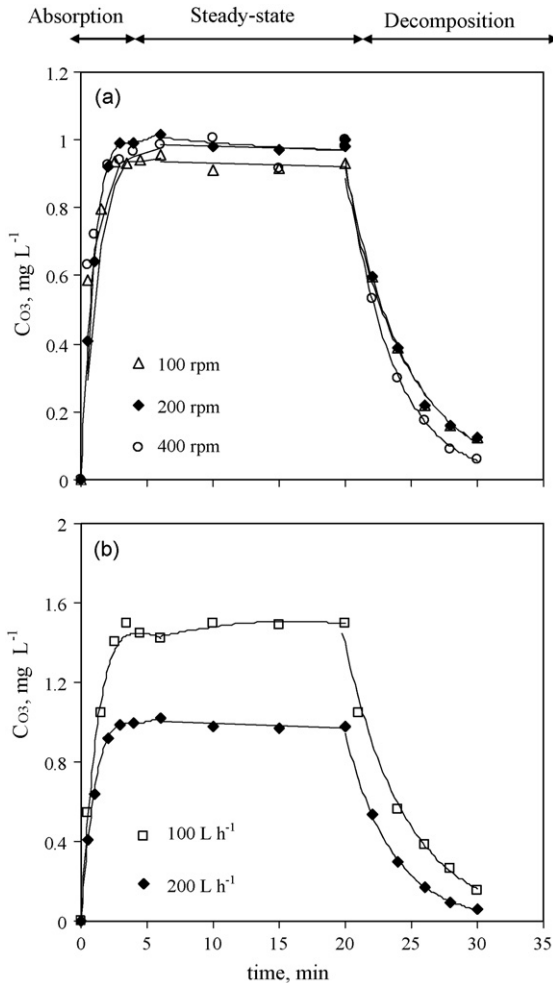
Fig. 1. Influence of stirring rate and inlet gas flow rate on the evolution of dissolved ozone concentration in organic-free aqueous solutions. Ozone mass flow $1.7\,g\,O_3\,h^{-1}$: (a) inlet gas flow rate $200\,L\,h^{-1}$; (b) stirring rate $200\,rpm$.

ozone concentration in steady state increased from 0.98 to $1.48\,mg\,O_3\,L^{-1}$ when the inlet gas flow rate decreased from 200 to $100\,L\,h^{-1}$. According to the Henry's law this fact is due to the increase in the ozone partial pressure from $0.4\,kPa$ to $0.8\,kPa$ when the inlet gas flow rate decreased from 200 to $100\,L\,h^{-1}$.

3.1.1. Ozone decomposition kinetic rate

An ozone mass balance in the reactor during decomposition period yields the following expression:

$$-\frac{dC_{O_3}}{dt} = r_d = k_d C_{O_3}^m \tag{1}$$

where C_{O_3} is the molar concentration of ozone in the bulk liquid phase, r_d the rate of ozone decomposition reaction, k_d the decomposition rate constant and m is the kinetic order. According to Refs. [6,9,10] it was assumed that dissolved ozone decomposed in aqueous solutions following first-order kinetics ($m = 1$). Eq. (1) can be integrated assuming that the initial ozone concentration in the decomposition period is $C_{O_3,SS}$, to yield:

$$C_{O_3} = C_{O_3,SS}\,e^{-k_d t} \tag{2}$$

being $C_{O_3,SS}$ the steady state concentration of ozone in the liquid phase. Eq. (2) can be used to evaluate decomposition rate constants by linear regression of ozone decomposition data shown in Fig. 1. Experimental values are listed in Table 1. The goodness of the fitting procedure (correlation coefficients r^2 were always higher than 0.99) corroborates the assumption of first-order decomposition kinetics. Decomposition rate constants range from 3.3×10^{-3} to $4.3 \times 10^{-3}\,s^{-1}$, which are in agreement with literature values reported for aqueous solutions with high concentration in bicarbonate ions (higher than $0.01\,mol\,L^{-1}$) at pH 8–10 [11].

3.1.2. Volumetric mass transfer coefficient

The volumetric mass transfer coefficient was determined from the experimental data shown in Fig. 1 obtained during the absorption period. The process of ozone absorption can be described by the following ozone mass balance, based on the assumptions that the changes of the ozone concentration in the gas phase during bubbling can be neglected as well as ozone decomposition follows a first-order kinetic:

$$\frac{dC_{O_3}}{dt} = k_L a_v(C_{O_3}^* - C_{O_3}) - k_d C_{O_3} \tag{3}$$

where $C_{O_3}^*$ is the equilibrium molar concentration of ozone in the liquid phase and $k_L a_v$ the volumetric mass transfer coefficient in the liquid phase. Eq. (3) can be integrated at the initial condition $t = 0$, $C_{O_3} = 0$, yielding the following expression [10]:

$$C_{O_3} = \frac{C_{O_3}^*}{1 + k_d/k_L a_v}\left\{1 - \exp\left[-\left(1 + \frac{k_d}{k_L a_v}\right)(k_L a_v t)\right]\right\} \tag{4}$$

The mass balance of ozone during steady state takes the form:

$$k_L a_v(C_{O_3}^* - C_{O_3,SS}) = k_d C_{O_3,SS} \tag{5}$$

Rearranging this expression:

$$\frac{C_{O_3}^*}{C_{O_3,SS}} = 1 + \frac{k_d}{k_L a_v} \tag{6}$$

Therefore, the steady state concentration of ozone in the bulk phase may not correspond to the equilibrium. Both are related through the decomposition rate constant and the volumetric mass transfer coefficient. Eqs. (4) and (6) can be fitted to the experimental data corresponding to the ozone absorption period by performing a non-linear analysis based on minimization of the sum of squares. As a result of such procedure, the values of the searched parameters ($k_L a_v$ and $C_{O_3}^*$) can be estimated. Values are summarized in Table 1. The statistical quality of regression is good ($r^2 > 0.99$). As can be seen, the coefficient $k_L a_v$ slightly increased from 0.012 to $0.017\,s^{-1}$ when the inlet gas flow rate increased from 100 to $200\,L\,h^{-1}$ maintaining constant stirring rate (200 rpm). This fact was due to the enhancement in mass transfer, as can be expected. It was not observed a remarkable influence of stirring rate on the volumetric mass transfer coefficient. The values of the volumetric mass transfer coefficient are consistent with those reported for stirred tank reactors, which range from 0.003 to $0.8\,s^{-1}$ [12]. It can also be observed that

Table 1
Mass transfer parameters corresponding to the ozonation of organic-free aqueous solutions

Q_{gas} (L h^{-1})	Stirring rate (rpm)	$C_{O_3,SS}$ (mg L^{-1})	$C^*_{O_3}$ (mg L^{-1})	$k_d \times 10^3$ (s^{-1})	$k_L a_v$ (s^{-1})
200	100	0.94 ± 0.02	1.11 ± 0.02	3.5 ± 0.6	0.020 ± 0.005
200	200	0.98 ± 0.14	1.13 ± 0.02	4.0 ± 0.1	0.017 ± 0.003
200	400	0.99 ± 0.16	1.19 ± 0.02	4.3 ± 0.3	0.021 ± 0.002
100	200	1.48 ± 0.08	1.99 ± 0.02	3.3 ± 0.8	0.012 ± 0.001

the value of ozone self-decomposition constant, k_d, was very small compared to the coefficient $k_L a_v$. On the other hand, gas phase resistance to mass transfer can be neglected due to the low solubility of ozone [13,14]. Therefore, the major resistance to mass transfer was assumed to be in the liquid side.

3.1.3. Ozone solubility

The equilibrium concentration of ozone was experimentally estimated as described above. Values are summarized in Table 1. As can be seen, very small differences were found and a mean value of 1.14 mg O$_3$ L^{-1} can be considered for an inlet gas flow rate of 200 L h^{-1}. The ozone equilibrium concentration increased considerably from 1.13 to 1.99 mg O$_3$ L^{-1} after reducing the inlet gas flow from 200 to 100 L h^{-1}, which was due to the higher ozone partial pressure in the inlet gas stream. As Henry's law was assumed for ozone dissolution in aqueous solutions, Henry's law constant, H_{O_3}, can be determined from its definition:

$$H_{O_3} = \frac{p_{O_3}}{C^*_{O_3}} \tag{7}$$

From the experimental data summarized in Table 1, a mean value of the Henry's constant of 18 kPa mol^{-1} m^3 at 25 °C and pH 8.7 was found. This value can be compared with those predicted from literature equations. From the work of Roth and Sullivan that fitted Henry's law constant as a function of pH and temperature [6], a value of 13 kPa mol^{-1} m^3 was obtained at 25 °C and pH 8.7. Equations for Henry's law constant as a function of temperature, pH and ionic strength for sodium phosphate solutions are available in literature [15]. The application of these equations led to a value of 15 kPa mol^{-1} m^3. The solubility of ozone in water in aqueous solutions of sodium chloride, potassium chloride, sodium sulfate and magnesium sulfate were also studied, estimating the Henry's constant on the basis of the Sechenov relation [9]. From this work, it was obtained a value of 10–11 kPa mol^{-1} m^3 at 25 °C in acidified solutions containing chloride ions or sulfate ions, respectively. Henry's law constant is a function of temperature, pH and ionic strength as well as the type of ions. The slight difference between experimental and predicted values using literature equations is probably due to the complex inorganic composition of the real effluent, containing bicarbonate, chloride and sulfate ions. Moreover, literature works were performed using aqueous solutions with different ionic composition that of molasses effluents. The complex inorganic content of the industrial wastewater recommended us to estimate solubility using organic-free solutions containing all salts present in the real wastewater.

3.2. Reaction parameters

Reaction parameters were determined from molasses wastewater ozonation experiments varying stirring rate and the inlet gas flow rate. Fig. 2 shows the evolution of wastewater color, measured as absorbance at 475 nm, with reaction time. As can be seen from the figure, color was effectively reduced. After 25 min reaction time, the percentage of color reduction was about 70–75%, increasing up to 85–87% after 40 min ozonation.

3.2.1. Stoichiometric factor

A previous study showed that wastewater color was due to the presence of melanoidins [2]. Melanoidin concentration in wastewater can be calculated according to the Lambert–Beer equation (a.u. = $\varepsilon C_M l$) that relates linearly absorbance (a.u.) and concentration (C_M) through the extinction coefficient (ε) if the length of the cuvette (l) is constant. The extinction coefficient was obtained from literature [1]. Values of ε at 470 nm were estimated for melanoidins synthesized from glucose/amino acid, ranging from 0.34 L mmol^{-1} cm^{-1} for glucose/alanine melanoidins to 0.94 L mmol^{-1} cm^{-1} for glucose/casein melanoidins. Since elemental composition of melanoidins depends strongly on the starting materials as well as the reaction conditions, it was used a value of ε of 0.65 L mmol^{-1} cm^{-1} corresponding to glucose/glycine system, monosaccharide and amino acid present in beet sugar juices in high concentration.

The stoichiometric factor (z) for the reaction between colorants (melanoidins) and ozone is defined as moles of ozone
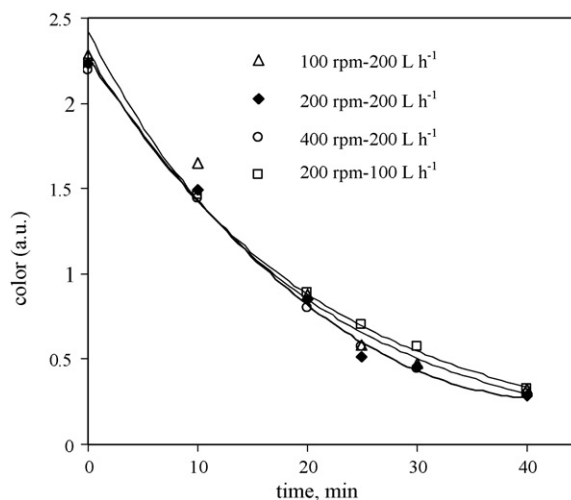

Fig. 2. Evolution of color with reaction time during ozonation of biologically pretreated molasses wastewater. Influence of stirring rate and inlet gas flow rate.

consumed per mole of melanoidin degraded. Assuming that ozone is only consumed by the coloring organic matter (M) in the wastewater through one irreversible reaction, the stoichiometric factor can be determined from the amount of ozone and colorants consumed at different reaction times:

$$zO_3 + M \rightarrow P$$
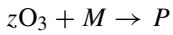
$$z = \frac{\Delta C_{O_3}}{\Delta C_M} = \frac{(F_{in} - F_{out})\Delta t}{(C_{M0} - C_M)V} \tag{8}$$

where F_{in} and F_{out} represent the molar flow rates of ozone at the reactor inlet and outlet, respectively, during a reaction period Δt; C_{M0} and C_M are the molar concentration of melanoidin at the start and end of that reaction period, respectively, and V is the reaction volume. Stoichiometric factor was determined from the evolution of absorbance at 475 nm in the experimental runs shown in Fig. 2. This parameter is needed to obtain the rate constant of the ozone–melanoidin decolorization reaction. Fig. 3 shows the evolution of the stoichiometric factor with reaction time. As can be seen, during the first 20 min of ozonation it was obtained an average value about 4 mol of ozone consumed per mol of melanoidin degraded. As reaction proceeds, the stoichiometric factor increased up to 12–14, which indicates that ozone was consumed by reactions with inorganic and non-colored organic compounds in wastewater. This fact can be explained as follows: after 20–25 min ozonation the concentration of functional groups responsible for color was removed to a reasonable extend as indicated the lower absorbance at 475 nm, which was reduced by about 70–75%. Then, there are less reaction partners for direct reactions between colorants and ozone molecules. In literature, data of the stoichiometric factor for ozone–melanoidin reaction are not available, so this kinetic parameter cannot be compared with values previously reported. In any case, z was considerably higher than the stoichiometric factor reported for azo dyes [16], where a ratio of 1 mol O_3/mol dye was found.
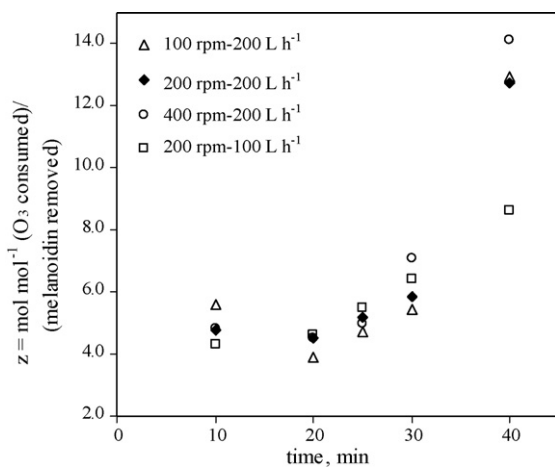

Fig. 3. Evolution with reaction time of the stoichiometric factor for the reaction between ozone and melanoidins in biologically pretreated molasses effluents. Influence of stirring rate and inlet gas flow rate.

3.2.2. Kinetic rate constant

The film theory was applied for determining the rate constants. During the experimental runs carried out with molasses wastewater dissolved ozone was not found, which suggested that wastewater decolorization was due to direct reactions between ozone and colorants. Due to the absence of dissolved ozone in the liquid bulk, the reactions can be considered to develop in the fast kinetic regime in the diffusion film. Moreover, the initial concentration of melanoidins in the liquid bulk (3.4×10^{-3} mol L^{-1}) was 100 times greater than the ozone equilibrium concentration ((2.5×10^{-5}–4×10^{-5} mol O_3 L^{-1}), so it can be considered that the reaction does not cause any significant depletion of colorants through the liquid film. This fact allows us to assume the regime to be fast of pseudo-first-order [17,18]. The kinetic regime can be corroborated determining the reaction factor (E). This parameter represents the ratio between the actual and maximum physical absorption rates of ozone. The parameter is defined as follows [19]:

$$E = \frac{F_{in} - F_{out}}{k_L a_v C_{O_3}^* V} \tag{9}$$

Assuming that the reactions between ozone and colorants develop in the fast and pseudo-first-order kinetic regime, the film theory establishes that $E = Ha$ and the following criterion is fulfilled: $3 < Ha < E_i/2$, where Ha is the Hatta number, which indicates the relative importance of the chemical reaction compared to the mass transfer. The Hatta number is defined as

$$Ha = \frac{1}{k_L}\sqrt{k_r D_{O_3} C_M} \tag{10}$$

being k_r the decolorization reaction constant and k_L the individual mass transfer coefficient in the liquid phase. The instantaneous reaction factor, E_i, can be evaluated by the following equation provided by the film theory:

$$E_i = 1 + z\frac{D_M}{D_{O_3}}\frac{C_M}{C_{O_3}^*} \tag{11}$$

where D_{O_3} and D_M are the diffusivity of ozone and coloring organic matter, respectively. These values were obtained from literature [19]: $D_{O_3} = 1.3 \times 10^{-9}$ m^2 s^{-1} and $D_M = 10 \times 10^{-10}$ m^2 s^{-1}. The latter correspond to the diffusivity of dissolved organic matter present in distillery wastewaters. Since it was assumed that ozone absorbed only reacts with the colored compounds through one irreversible reaction, the rate of colorant disappearance equals the ozone absorption rate:

$$N_{O_3}a_v = z\left(-\frac{dC_M}{dt}\right) = k_L a_v C_{O_3}^* E \tag{12}$$

With the condition $E = Ha$ and combining Eqs. (10) and (12), the following equation can be obtained after integration:

$$\sqrt{C_M} = \sqrt{C_{M0}} - \left(\frac{k_L a_v}{2z k_L}C_{O_3}^* \sqrt{k_r D_{O_3}}\right)t \tag{13}$$

Table 2
Kinetic reaction parameters according to film theory for the reaction between ozone and melanoidins in biologically pretreated beet molasses wastewater

Q_{gas} (L h^{-1})	Stirring rate (rpm)	$k \times 10^{-7}$ (L mol^{-1} s^{-1})	E	Ha	E_i
200	100	0.9	17	20	470
200	200	1.3	20	23	450
200	400	3.8	15	14	420
100	200	0.6	14	16	250

According to Eq. (13), a plot of $(C_M)^{1/2}$ versus reaction time should lead to a straight line whose slope is b:

$$b = -\frac{k_L a_v}{2zk_L} C_{O_3}^* \sqrt{k_r D_{O_3}} \qquad (14)$$

Fig. 4 shows the evolution of $(C_M)^{1/2}$ versus reaction time for the experimental runs shown in Fig. 2. Data correspond to the first 25 min reaction, when decolorization rate is higher and direct reactions between ozone molecules and colorants are more predominant. As can be observed, experimental points lie around straight lines, corroborating the previously supposed fast pseudo-first-order kinetic regime. The values of slopes were deduced from least-square analysis. Values ranging from 1.7×10^{-5} to 2×10^{-5} (mol L^{-1})$^{0.5}$ s^{-1} were obtained. The rate constant k_r can be determined from the slope values through Eq. (14). Table 2 summarizes the rate constants. The volumetric mass transfer coefficient in the liquid phase, $k_L a_v$, was experimentally determined as shown above. Interfacial areas, a_v, were predicted using correlations for stirred vessel reactors [20]. To prove that the fast and pseudo-first-order absorption kinetic regime initially assumed is appropriate, the Hatta number and the instantaneous reaction factor were calculated by means of Eqs. (10) and (11), respectively. The Ha number and E_i values were obtained for all the experiments at the initial times when it can be assumed that ozone only reacts with colorants. The reaction factor was calculated from the molar flow rates of ozone at the reactor inlet and outlet (Eq. (9)).

As can be seen from Table 2, E values were always higher than 2, which confirm the fast absorption kinetic regime for ozone. Since $E \approx Ha$ and the criterion $3 < Ha < E_i/2$ was fulfilled, it can be assumed that decolorization reactions develop in the fast pseudo-first-order kinetic regime with a rate constant ranging from 0.6×10^7 to 3.8×10^7 L mol^{-1} s^{-1}. It can also be observed that decolorization rate constants increase slightly with increasing stirring rate and the inlet gas flow rate. Due to the lack of references relating to the ozonation kinetics of melanoidins, no comparison could be made for the reaction rate constants. In any case, kinetic constants are in the same range as those reported for azoic colorants at 20 °C: 10^6–4×10^7 L mol^{-1} s^{-1} [16,21].

4. Conclusions

In this study, physico-chemical parameters corresponding to the decolorization reaction between ozone and melanoidins in molasses fermentation effluents have been determined. The application of film theory enables to estimate the kinetic rate constant, the Hatta number and the enhancement factor. From the results, it was shown that ozone reacts with colorants in molasses wastewater through direct reactions proceeding within the film in a fast and pseudo-first-order kinetic regime. Therefore, reactors with high specific interfacial areas are highly recommended for decoloring molasses processing effluents with ozone. The kinetic rate constants were evaluated at pH 8.7 and 25 °C, ranging from 0.6×10^{-7} to 3.8×10^{-7} L mol^{-1} s^{-1}, depending on stirring rate and the inlet gas flow. The stoichiometric factor was also determined: 4 mol of ozone per mol of melanoidin degraded. It should be noted that kinetic parameters were determined assuming than ozone was consumed by dissolved coloring organics through one irreversible reaction. However, during the process ozone can be consumed by other organic and inorganic wastewater components in reactions that are difficult to distinguish. A more complete study on ozonation of synthetic solutions of melanoidins must further be performed in order to favor the reaction of ozone with the target chemical over side reactions.
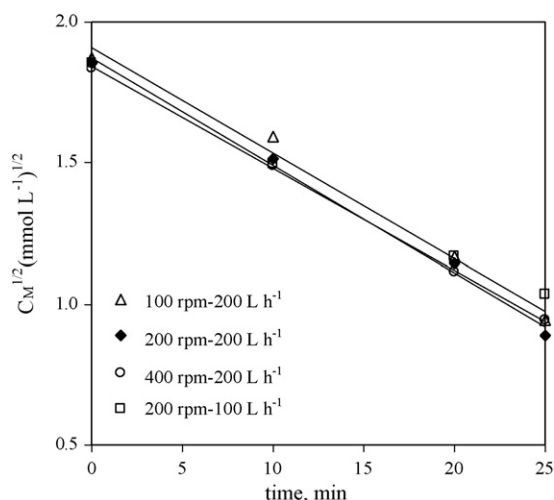

Fig. 4. Verification of Eq. (13) for a fast pseudo-first-order reaction in the case of decolorization of biologically pretreated molasses wastewater with ozone.

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