Electrochemical generation of ozone using a PEM electrolyzer at acidic pHs

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Abstract

This work focuses on the electrochemical production of ozone at acidic pHs, evaluating the influence of the salts in the electrolyte, temperature and pressure on the efficiency of its production. Results demonstrate that electrolysis with electrolytes containing perchlorate salts allow obtaining higher concentrations of ozone than electrolytes containing sulfates. Adding to that, the increase in the operation pressure and the decrease in temperature have a positive effect on the production of ozone. This indicates that not only the oxidation of water, but also the oxidation of oxygen is important to explain the electrochemical production of ozone. A simple model considering all these processes is formulated and validated with the experimental results that allow explaining the fundamentals of ozone production in acidic conditions.

Keywords

Electro-ozonizer; ozone; electrolysis; pressurized cells

Highlights

- Cell pressurization can increase ozone production in electrochemical cells

- Higher ozone production in electrolytes with perchlorates as compared with sulfates
- Acidic pHs improve production of ozone, which also develops from oxygen
- Low temperatures improve production and accumulation of ozone

Symbols

I	Current intensity
F	Faraday's constant
η_{a1}	Proportion of electric current that is used to produce ozone
η_{a2}	Proportion of electric current that is used to produce oxygen
η_{a3}	Proportion of electric current that is used to produce ozone from oxygen
η_{a4}	Proportion of electric current that is used to produce the anodic formation of peroxo scavenger species
η_{a5}	Proportion of electric current that is used to direct oxidation of organics
η_{c1}	Proportion of electric current that is used to produce the cathodic formation of peroxo scavenger species
η_{c2}	Proportion of electric current that is used to reduce water into hydrogen
k_3	Constant rate of decomposition of ozone
k_4	Constant rate of decomposition of ozone with peroxo species
k_8	Constant rate of oxidation of organics by ozone
k_9	Constant rate of oxidation of organics by scavenger
$[S_1]$	Ozone concentration
$[S_2]$	Oxygen concentration
$[S_3]$	Peroxo species concentration
$[S_4]$	Organic concentration

1. Introduction

Ozone is one of the most powerful oxidants with real applicability in the remediation of polluted wastewater. In addition to its very high oxidation potential, reduction products formed during its application are unarmful, which becomes a very important aspect, especially when comparing this oxidant with others such as chlorine, which unfortunately as a result of its application, leaves molecules that are more hazardous than the parent compounds [1,2]. Its main drawbacks are high production costs, typically associated to the very high voltages applied in the electric discharge production method (often known as corona discharge), with a huge amount of energy dissipated as heat [3–5], and the low solubility of the ozone gas into the liquid where its action is required.

In trying to find alternatives to corona discharge, one of the most promising processes is the electrolytic production of ozone [6–9]. This process has been assessed in many recent works and some companies are selling devices that promote the formation of ozone even in liquids with very low conductivity [10–12]. Many of these devices are based on the use of diamond electrodes. These electrodes have demonstrated important advantages for the ozone electrogeneration, including their inert surface with a low adsorption capacity, corrosion stability, a wide potential window and very high overpotential for oxygen, which is an important aspect in the electrolytic materials selected for ozone generation due to the competition with oxidation of water to oxygen. Also the design of new cell concepts with an improved mass transfer condition, such a PEM (Polymer Exchange Membrane) electrolyzes has shown a good alternative [13–20]. To begin with, this technology needs lower cell voltages, which entail lower energy costs and in addition, ozone is produced directly into the liquid, which is a very important advantage considering that the solubility of ozone in water is extremely low and its absorption into the liquid is the bottleneck of corona discharge technology [5,21].

The electrochemical production of ozone is known to develop from the oxidation of water on the surface of the anode of electrochemical cells [22] according to equation 1. This reaction competes with the oxidation of water to oxygen, which needs lower potentials ($E^\circ = +1.23$ V vs $E^\circ = +1.51$ V) and only a four electron-transfer, instead of the six required for the formation of ozone [23,24]. The formation of ozone from oxygen according to a two-electron reaction shown in eq 3 is also reported, though in the existing literature this

reaction is not always considered feasible. Also, the oxidation of water to ozone competes with the production of hydrogen peroxide (eq 4), which is the least promoted reaction as it is only feasible within a narrow range of cell voltages.

In most of the works reported in the literature[25–29], the electrolytic production of hydrogen peroxide is not based on the anodic oxidation of water but on the cathodic reduction of oxygen as shown in eq. 5. However, this reduction reaction competes with the production of hydrogen (eq. 6) [30], which is less favored at high cell voltages. Hence, there are many potential reactions developing at a time in the electrochemical cell and they are not the only possibilities for the formation of species, as the ions contained in the electrolyte can also be oxidized or reduced and adding to that, in bulk, the different species can interact or decompose, as shown by eqs 7 and 8, which are representative of hundreds of reactions that may occur in the solution, making the production of ozone by electrochemical technology a tricky problem, because of the very **complex** reactivity of the system.

Hence, electrochemistry and chemistry of oxygen-containing species in electrolytic systems aiming to promote the production of ozone are rather complex and should be the key to find out an effective production technology for ozone. In a previous paper [31], a model was proposed to explain the performance of an electrolyzer producing ozone at near-neutrality pH conditions. This model helped to explain the evolution of ozone during continuous and discontinuous processes as well as the influence of current density on the production of this compound. Reactions such as Eq. 7 were found to be of extreme

importance, because they made it possible to understand why the amount of ozone accumulated could not be further increased.

Considering this background, the present paper aims to enhance our previous model and improve the understanding of ozone production, considering that it cannot be formed only by oxidation of water, but also by oxidation of oxygen and how by means of supporting electrolytes such as perchlorate, which cannot lead to the formation of oxidants (avoiding or minimizing scavenging reactions of ozone), this production can be enhanced. It is also intended to find out if dissolved oxygen plays a significant role on the production of ozone; the effect of the pressure and temperature is evaluated. As with all gases, the dissolved concentration of oxygen is known to increase with pressure and decrease with temperature; thus, in case of a direct oxygen oxidation to ozone, the modification of both parameters in the right direction should show a positive effect on ozone production.

2. Materials and Methods

2.1 Reagents and Chemical

Double de-ionized water (Millipore Milli-Q system, resistivity: $18.2 \mu\Omega \text{ cm}^{-1}$ at 25 C) was used to prepare water solutions. Sulfuric acid (H_2SO_4) and perchloric acid (HClO_4) are used as electrolyte. Sodium hydroxide was used to change the pH up to the desired value. These reagents were of analytical grade and provided by Sigma-Aldrich. Methanol and formic acid (HPLC grade) were used in the preparations of the mobile phase for the HPCL analysis (Sigma-Aldrich, Spain). Clopyralid (3,6-Dichloro-pyridine-2-carboxylic acid) used for organic degradation tests was also supplied by Sigma-Aldrich.

2.2 Experimental setup

The experimental setup used in this work is described elsewhere [32]. The experiments were carried out in a bench-scale plant equipped with a commercial CONDIAPURE® cell. This electrochemical reactor was designed and marketed by the company CONDIAS GMBH (Izhehoe, Germany). The same solution enters in the cell and floods the electrodes and the membrane. It is not a separate cell, the membrane has the function of joining the electrodes and closing the ionic circuit, allowing the protons to go from the anode to the cathode. The cell is equipped with two diamond electrodes with an electrode surface of

2.4. Experimental procedure

The electrolysis experiments were performed in a commercial CONDIAPURE® cell in continuous and discontinuous mode, using a solution of pH 3 either with H₂SO₄ or HClO₄ and applying a current of 10 A for both operation modes. For the test in continuous mode, the solution flows from the reservoir tank to the cell and is collected to a different tank. In discontinuous operation, the solution is recirculated through a pressurized reservoir tank and the CONDIAPURE® cell at a constant flow of 150 L h⁻¹. For the organic pollutant oxidation tests, the solution was prepared with 100 mg L⁻¹ of clopyralid. The temperature was controlled by a heat exchanger and was kept between 20 °C and 13°C.

3. Results and Discussion

The influence of the supporting electrolyte, mode of operation, presence of organic pollutants, concentration of oxygen and temperature on the production of ozone at acidic pH will be assessed. Figures 2-7 display the predictions of two models, which are described and discussed in the final part of this section. The predictions in blue correspond to a model developed in a previous work [31] for the production of ozone at mild pH values, while lines in black correspond to a model adapted for the production of ozone at acidic pH.

Influence of the supporting electrolyte.

Figure 2 shows the effect of the composition of the supporting electrolyte on the production of ozone in continuous mode when a current of 10A is applied, by comparing an aqueous solution containing sulfuric and perchloric acids. As observed, the concentration of ozone increases rapidly in both cases, and then it reaches the steady state value in under 1 minute. Then, the concentration is maintained. Since the process is continuous, the production of ozone can be obtained multiplying the flowrate by the concentration, which is 148 mg h⁻¹ in the case of using an electrolyte with sulfuric acid, and 158 mg h⁻¹ in the case of using an electrolyte with perchloric acid. Thus, the concentration reached is slightly higher in the second case and at first, this difference should be explained in terms of the production of peroxo-compounds (such as monoperoxosulfuric acid) and the interaction of these oxidants with ozone according to reaction 9. In this regard, a previous work studied the generation of hydroxyl radical

(•OH) and sulfate radical ($\text{SO}_4^{\bullet-}$) by the reaction of ozone (O_3) with peroxymonosulfate (PMS; HSO_5^-) and demonstrated that the reaction between the anion of PMS (i.e., SO_5^{2-}) and O_3 is primarily responsible for driving O_3 consumption [33]

Fig 2. Electrolyte influence on the production of ozone in continuous mode, ○ H_2SO_4 , pH 3.60; ◆ HClO_4 , pH 3.80; – model prediction in H_2SO_4 , pH 3.60; --- model prediction in HClO_4 , pH 3.80 (4 L min^{-1} , 20°C , 10A). Model 1 (mild pHs): blue lines, Model 2: black lines.

Influence of the operation mode.

Figure 3 show the results obtained in discontinuous operation mode. Concentration in the liquid follows a typical trend for ozone electrochemical production, with a rapid increase, which ends up in a maximum value, from which a decay in the concentration is observed. This trend is not the typically obtained in the discontinuous electrolytic production of other oxidants, for which the initial fast increase is followed by stabilization, indicating that the formation and destruction rate of oxidants is balanced. Conversely, it can only be explained by considering the formation of third species which act as **scavengers** of the formed ozone. It is already known [31] that oxidants can easily interact with each other decomposing and forming other species with various oxidation capacities. This way, the

interaction of ozone with hydrogen peroxide (eq 7) or with monoperoxosulfuric acid (eq 9) promotes the formation of radicals, which following different mechanisms lead to the formation of oxygen. This can explain the higher destruction rate observed in the last stage in supporting electrolytes containing sulfuric acid, as in the case of electrolytes formulated with perchloric acid, chlorine is at the highest oxidation state and consequently no other oxidant is expected to be formed. Just hydrogen peroxide, which can also be produced anodically (eq 4) or cathodically (eq 5), also in electrolytes with sulfuric acid. It is important to bear in mind that the interaction between oxidants leads to the formation of powerful radicals. As a matter of fact, the formation of these radicals has been found to be very important in the success of a number of advanced oxidation processes, greatly improving the efficiency of the processes. However, when these radicals do not find other compound to be oxidized, they are known to recombine to form oxygen or even propagate the destruction of ozone in chain reactions. Owing to this, regarding the electrolyte, the best results are obtained when perchlorate is the salt contained in the electrolyte. These results are better than those for sulfates. In fact, the rate of decomposition obtained from the slopes of the last decay stage in sulfuric acid media (0.120 mg h^{-1}) is 2 times higher than in the case of perchloric acid media (0.060 mg h^{-1}).

Production rates in continuous mode are 148 mg h^{-1} and 158 mg h^{-1} in H_2SO_4 and HClO_4 , respectively, while in discontinuous mode, they are 4.36 mg h^{-1} and 4.7 mg h^{-1} in H_2SO_4 and HClO_4 , respectively; this proves that the best operation mode is continuous.

To explain why discontinuous mode is not the best for the production of ozone, it is important to bear in mind that ozone is not only destroyed electrochemically, but also by other species which are simultaneously formed in the electrolyte. Thus, in order to promote a large production of ozone, it is important to avoid the formation of these scavengers of ozone and, despite information from this operation mode is not as relevant as initially expected, it indicates that operation in continuous mode can be one way to produce more ozone, trying to avoid the negative effects of the continuous formation of competing oxidants on the electrolyte.

Fig 3. Electrolyte influence on the production of ozone in discontinuous mode, ○ H₂SO₄, pH 3.60; ◆ HClO₄, pH 3.80; – model prediction in H₂SO₄, pH 3.60; --- model prediction in HClO₄, pH 3.80 (4 L min⁻¹, 20°C, 10A). Model 1 (mild pHs): blue lines, Model 2: black lines.

Another important observation comes from the comparison of the formation of ozone at neutral and acidic conditions (Figure 4) using sulfuric acid and sulfate mixtures. As noticed, production at neutral conditions is much less important. This can be explained because the production of peroxospecies at acidic conditions is not as favored as in neutral conditions. Thus, at acidic conditions monoperoxosulfuric (H₂SO₅) acid is expected, while at neutral, peroxodisulfate (S₂O₈²⁻) is the key oxidant and so the decomposition of ozone should develop following reaction 12.

In previous studies carried out with a similar species (peroxophosphates) [34], it was demonstrated that the instability of monoperoxo acids is much higher than that of diperoxosalts. It leads to pseudo-steady state concentrations that are several folds below and, because of that, their lower production should lead to a lower influence on ozone destruction. When comparing the apparent destruction rates (slope of the last stage), it is important to notice that this rate is higher in the case of peroxodisulfate than in the case of monoperoxosulfuric acid.

Figure 4. Effect of pH on the production of ozone in discontinuous mode. ○ H₂SO₄, ◆ Na₂SO₄ (150 L h⁻¹, 20°C, 10A). – model prediction in H₂SO₄, --- model prediction in Na₂SO₄. Model 1 (mild pHs): blue lines, Model 2: black lines.

Influence of dissolved oxygen concentration.

It is typically expected that ozone is only formed from the oxidation of water according to the reaction in Eq. 1. To verify if oxygen concentration has any influence, two parameters with direct influence on such concentration were modified: pressure and temperature. Obviously, if oxygen is a raw matter in the production of ozone, the increase in pressure should have a positive effect on results because the solubility of a gas depends directly on pressure. It is also expected that a decrease in temperature affects positively, since the solubility of gases into liquids increases as temperature drops.

Figure 5 shows the effect of pressure for both electrolytes by comparing the production of ozone at atmospheric pressure and at 2 bars in tests made in discontinuous operation. Two important observations can be made: first, the same trends observed for the influence of the salt contained in the electrolyte are maintained at higher pressures; second, pressure has a very positive effect on the results and allows reaching concentrations that are 1 mg L⁻³ above in relation to the non-pressurized system.

As for the rates of decomposition (calculated with the slope of decay), it is important to notice there are no significant differences in the values obtained for each electrolyte.

Fig 5. Pressure influence on the production of ozone in discontinuous mode, ○ H_2SO_4 ; ◆ HClO_4 ; – model prediction in H_2SO_4 ; --- model prediction in HClO_4 (150 L h^{-1} , 10 A). Model 1 (mild pHs): blue lines, Model 2: black lines. Without pressure (black symbol) and 2 bar (grey symbol).

The solubility of oxygen depends linearly on pressure, though this is not the case for ozone production, which means that an increase in the oxygen available for surface electrochemical process can also be promoting the formation of hydrogen peroxide (as demonstrated in previous works by our group [25,35–37]) and hence, the decomposition of ozone with the formation of peroxone reagent, which leads to the formation of hydroxyl radicals, and then to the loss of oxidation capacity via the formation of more stable oxygen. Then, increasing oxygen by operating at a higher pressure has two opposite effects on the production of ozone: positive from the viewpoint of ozone production; negative from the standpoint of production of other competing species, causing the destruction of ozone.

Figure 6 shows the effect of temperature. A decrease of 7°C in temperature has a positive effect on both electrolytes that allows increasing the production by more than 0.5 mg L^{-3} . Again, the rates of ozone decomposition are kept for perchlorates and persulfates (0.116 vs 0.117 mg h^{-1}), indicating that the decomposition rate is not apparently affected by this decrease in the temperature.

Fig 6. Temperature influence on ozone concentration in discontinuous mode, $\circ$ H_2SO_4 ; $\blacklozenge$ HClO_4 ; — model H_2SO_4 ; --- model HClO_4 , at 20°C (black and dark blue symbols and lines) and 13°C (grey and light blue symbols and lines) (150 L h^{-1} , 10A). Model 1 (mild pHs): blue lines, Model 2: black lines.

Degradation of pollutants.

Figure 7 compares the ozone produced at room pressure and at 5 bar in the presence and absence of the pollutant clopyralid. As expected, operating at higher pressures leads to a higher production of ozone but again, the increase in the production observed is much lower than that expected with an increase of 5 times in the concentration of raw oxygen, pointing out the influence of ozone **scavengers** on its production. Moreover, it is noticed that the presence of clopyralid leads to a much lower concentration of ozone, indicating that this oxidant is consumed in the oxidation of clopyralid.

Fig 7. Pressure influence on ozone production in presence (black symbols) and absence (grey symbols) of Clopyralid in discontinuous mode. ■ 5 bar, ○ atmospheric pressure (150 L h⁻¹, 10 A, 100 mg L⁻¹ Clopyralid). Model 1 (mild pHs): blue lines, Model 2: black lines.

As a consequence, the concentration of clopyralid and TOC decreases, being this decrease greater at higher pressures (Figure 8). Note that the solubilization of gases increases linearly with pressure and it also improves at lower temperatures. This explains the positive effect of working under pressurization. A very important remark on this figure is that perhaps much of the information published regarding the electrochemical oxidation of different species with diamond anodes should be explained in terms of the production and further activation of ozone.

Fig 8. Mineralization (full symbols) and clopyralid removal (empty symbols) during electro-ozonation at 5 bar (●) and atmospheric pressure (■). — model 5 bar, --- model atmospheric pressure (150L h⁻¹, H₂SO₄ 10 A, 100 mg L⁻¹ of Clopyralid)

Phenomenological model.

Blue lines plotted in figures 2 to 7 were obtained by applying a phenomenological model for the formation of ozone at mild pH conditions (model 1), which considers the processes included in the Pearson's matrix shown in Table SM1. This first model was proposed in a previous manuscript [31], trying to explain the production of ozone at mild pH conditions according to experimental observations and it was found to very satisfactorily because it reproduce the behavior of electrolytic ozone production in continuous and discontinuous modes and also the influence of current density.

However, as noticed in all these figures, the blue lines are far from the experimental results obtained in this work, indicating that the model failed this time, when the pH of the electrolyte is more extreme. In fact, the observed experimental productions of ozone cannot be reached even considering extreme values for parameter η_{a1} . As discussed in the previous sections, this can be explained in terms of the formation of ozone from the oxidation of oxygen according to eq 1.

Taking this effect in consideration, a new model was formulated. The Pearson's matrix for this model is shown in Table 1. Simulations obtained with this new model (model 2) are the black lines shown in Figures 2 to 7, which clearly fit much better the experimental results. In addition, regression coefficients for the previous and the new models as well as the experimental versus the modelled plot for all results shown in this work are in Figure 9, where the much better reproducibility reached by considering the formation of ozone, not only from water but also from oxygen, is actual proof of the relevance of these mechanisms, despite the conclusions of previous works, in which by means of isotope-based techniques it was proposed that ozone can only be produced from the six-electron transfer oxidation of water [22]

Table 1. Pearson's matrix of the model proposed for ozone production at acidic pH conditions

Process/species	S ₁ O ₃	S ₂ O ₂	S ₃ scavenger	S ₄ Organic	S ₅ H ₂	S ₆ H ₂ O	S ₇ scavenger precursor	Kinetics
P0: oxygen transfer from		+1						$k_L A ([O_2]_{sat} - [O_2]_1)$

atmosphere by aeration								
P ₁₋₁ : Electrochemical production of ozone from water	+1					-1		$\frac{I}{6F}\eta_{a1}$
P ₁₋₂ : Electrochemical production of ozone from oxygen	+1	-1						$\frac{I}{2F}\eta_{a3}$
P ₂ : Electrochemical production of oxygen		+1				-1		$\frac{I}{4F}\eta_{a2}$
P ₃ : Decomposition of ozone	-1	+1						$k_3[S_1]$
P ₄ : Decomposition of ozone with peroxo species	-1		+1					$k_4[S_1][S_3]$
P ₅ : Cathodic formation of scavenger species		+	+1					$\frac{I}{2F}\eta_{c1}$
P ₆ : Reduction of water to hydrogen					1	-1		$\frac{I}{2F}\eta_{c2}$
P ₇ : Anodic production of scavenger species			+1			-1	-1	$\frac{I}{zF}\eta_{a4}$
P ₈ : Oxidation of organics by ozone	-1			-1				$k_8[S_1][S_4]$
P ₉ : oxidation of organics by scavengers			-1	-1				$k_9[S_3][S_4]$
P ₁₀ : Direct electrochemical oxidation of organics				-1				$\frac{I}{zF}\eta_{a5}$

As noticed in all figures, the model fits well in all situations, which allows confirming the assumptions upon which it is based. Values of the parameters, collected in Table 2 and Table SM2, were fitted by trial and error trying to fit simultaneously all the cases studied. As observed, it is possible to describe all the cases with a single set of values, which gives robustness to the formulation made.

Regarding the values used for the fitting, ozone decomposition rate constants k_3 and k_4 are kept constant for the experiments at 20°C, though when temperature decreases 7°C these constants decrease by 30% because ozone stability is improved. All other chemical rate constants are kept in the same values in all cases. Regarding the anodic and cathodic efficiencies of the processes described above, these show influence of pressure, temperature and electrolyte, the efficiency of ozone production from water η_{a1} increases with the electrolyte, being higher when working with HClO₄. On the other hand, when working with pressure (increasing oxygen solubility), the efficiency of ozone production from oxygen η_{a3} increases and is greater than the efficiency of ozone production from water η_{a1} . Albeit, when the temperature of the system is lowered to 13°C, these make it equal or slightly higher the efficiency of ozone production from water η_{a1} . In terms of production efficiency of scavenger species η_{a4} , this is only produced when working with H₂SO₄ and it varies with the pressure and temperature of the system. Moreover, it is observed that an increase in pressure does not prevent the formation of scavenger species, but the drop in temperature allows reducing its production efficiency η_{a4} .

In terms of cathodic efficiency, these are constant in all cases η_{c1} η_{c2} . When an organic compound is present in the medium, the production efficiencies of ozone from water η_{a1} remain the same, as the process without pollutant, and also the production efficiencies of scavenger species, only the efficiency of oxygen production and ozone production from oxygen underwent changes because the organic pollutant can also be degraded directly on the anode. The anodic oxidation efficiency of the compound decreases when working with pressure, because as mentioned above, pressure favors the formation of ozone from oxygen, increasing thus η_{a3} .

Table 2. Fitting parameters obtained in this work for the simulations shown in figures 2 to 7.

Operation mode	Electrolyte	P (atm)	T(°C)	[S ₄] ₀	k ₃ (s ⁻¹) 10 ⁻⁴	k ₄ (s ⁻¹) 10 ⁻⁴	k _{LA} (s ⁻¹) 10 ⁻³	k ₈ (s ⁻¹) 10 ⁻⁵	k ₉ (s ⁻¹) 10 ⁻⁴	η_{a1}	η_{a2}	η_{a3}	η_{a4}	η_{a5}	η_{c1}	η_{c2}	r ² model 1
continuous	H ₂ SO ₄	1	20	0	5.1329	7.3713	0.004	1.15	5.55	0.3	0.2	0.3	0.3	0	0.2	0.8	0.92
discontinuous	H ₂ SO ₄	1	20	0	5.1329	7.3713	0.004	1.15	5.55	0.3	0.2	0.3	0.2	0	0.2	0.8	0.80
discontinuous	H ₂ SO ₄	2	20	0	5.1329	7.3713	0.004	1.15	5.55	0.3	0.2	0.35	0.15	0	0.2	0.8	0.87
discontinuous	H ₂ SO ₄	2	13	0	3.1636	5.3713	0.004	1.15	5.55	0.35	0.2	0.35	0.1	0	0.2	0.8	0.90
discontinuous	H ₂ SO ₄	1	20	100	5.1329	7.3713	0.004	1.15	5.55	0.3	0.15	0.15	0.2	0.2	0.2	0.8	0.80
discontinuous	H ₂ SO ₄	5	20	100	5.1329	7.3713	0.004	1.15	5.55	0.35	0.15	0.25	0.15	0.1	0.2	0.8	0.80
continuous	HClO ₄	1	20	0	5.1329	7.3713	0.004	1.15	5.55	0.45	0.2	0.35	0	0	0.2	0.8	0.94
discontinuous	HClO ₄	1	20	0	5.1329	7.3713	0.004	1.15	5.55	0.45	0.2	0.35	0	0	0.2	0.8	0.90
discontinuous	HClO ₄	2	20	0	5.1329	7.3713	0.004	1.15	5.55	0.38	0.18	0.44	0	0	0.2	0.8	0.83
discontinuous	HClO ₄	2	13	0	3.1636	5.3713	0.004	1.15	5.55	0.45	0.15	0.4	0	0	0.2	0.8	0.92

The figure 9 shows the correlation between the experimental data and model data for the model 1 (blue) and 2 (black) described previously, proving that the model 2 best describes the process in acid conditions.

Fig 9. Experimental versus simulation results of model 1 and 2, Model 1 (mild pHs): blue, Model 2: black continuous H₂SO₄, △ continuous HClO₄, ● discontinuous H₂SO₄, ■ discontinuous HClO₄, ▲ discontinuous H₂SO₄, 2 Bar, 20°C, ◆ discontinuous HClO₄, 2 Bar 20°C, X discontinuous H₂SO₄, 2 Bar, 13°C, + discontinuous HClO₄, 2 Bar, 13°C, ○ H₂SO₄, 2 Bar, with Clopyralid, □ H₂SO₄, without Clopyralid, ◇ TOC removal.

Conclusions

From this work, it can be concluded that the electrochemical production of ozone at acidic pHs can be improved by operating at higher pressures and lower temperatures. In the first case, owing to the higher concentrations of dissolved oxygen reached; in the second, because of an increase in ozone stability. It has also been verified that electrochemical production is higher in electrolytes containing perchlorate instead of sulfate, since perchlorates are not precursors of species that may act as ozone scavengers. To understand the formation of ozone in acidic conditions, not only its formation from water but also from oxygen is needed. Thus, a simple phenomenological model, with only few adjustable parameters, can successfully explain all the observations and it helps to highlight the differences between the operation of electro-ozonizers at mild or acidic conditions

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