Electrochemical incineration of vinasse in filter-press-type FM01-LC reactor using 3D BDD electrode

J. L. Nava, A. Recéndiz, J. C. Acosta and I. González

ABSTRACT

This work shows results obtained in the electrochemical incineration of a synthetic vinasse with initial chemical oxygen demand (COD) of 75.096 g L⁻¹ in aqueous media (which resembles vinasse industrial wastewater). Electrolyses in a filter-press-type FM01-LC electrochemical reactor equipped with a three-dimensional (3D) boron doped diamond electrode (BDD) were performed at Reynolds values between \( 22 \leq Re \leq 109 \), and a fixed current density of 10 mA cm⁻². The electrochemical incineration achieved up to 97\% in vinasse mineralization with current efficiencies that surpass unity and energy consumption of 168 KW-h m⁻³, at \( Re = 109 \). The mineralization of vinasse indicates that such degradation occurs via hydroxyl radicals formed by the oxidation of water on the BDD surface. Experimental data revealed that hydrodynamic conditions slightly influence the vinasse degradation rate and current efficiency, indicating that the oxidation involves a complex pathway.

Key words | alcohol wastewater, BDD electrodes, degradation of organics, FM01-LC reactor, vinasse

INTRODUCTION

Vinasses are residues from fermentation and distillation processes taking place in industrial plants that produce ethyl alcohol (Martin et al. 2003; 2005) and wines (Benítez et al. 2000). It is estimated that during the production of 1 kg of anhydrous alcohol between 16 and 124 L of vinasse are generated. These residues have high concentrations of organic matter expressed in terms of the chemical oxygen demand (COD) whose values range between \( 30 < \text{COD} < 150 \) g L⁻¹. Some organic substances contained in vinasses include alcohols, aldehydes, phenols, carboxylic acids, esters and non-fermented sugars.

It has been reported that when concentrated vinasses are irrigated into agricultural soils, they usually modify alkalinity and manganese concentration in the soil, thereby destroying cultures (Cirilo et al. 2007). This is due to high COD concentrations; however, if the amounts of these vinasses are controlled or well diluted, they can be used in agricultural activities. On the other hand, discharge of these residues to recipient water bodies, such as rivers, has a damaging ecological impact on water life (Cortez et al. 1997).

Biological treatment of vinasses employs fungi or microorganisms that feed on organic matter and thus decrease their COD. These processes use either anaerobic reactors, where biogas is recovered as a product, or aerobic reactors (Rao 1972; Sheehan & Greenfield 1980; Vlyssides & Zouboulis 1993; Benítez et al. 2000; Martin et al. 2003, 2005; Pérez García et al. 2005; Pant & Adholeya 2007; Singh et al. 2008). Such biological treatment partially oxidizes the alcohols, aldehydes, carboxylic acids, esters and sugars; however, it is little effective in phenol degradation, for which reason the treated vinasses are sometimes even more hazardous (Vlyssides & Zouboulis 1993; Singh et al. 2008). In addition, the above treatments require long
treatment times (Pérez García et al. 2005) and are usually carried out in stabilization lagoons that occupy huge land extensions.

Another approach to vinasse treatment is represented by Fenton reagent (Utset et al. 2000; Agladze et al. 2007), however this treatment focuses on oxidizing organic matter at low concentration and the reported efficiencies are poor.

Recently, electroincineration processes, using dimensionally stable anodes (DSA) have shown their convenience for organic matter degradation. Many investigations have been carried out on materials, such as RuO2, PbO2 and SnO2, employed as anodes, for the degradation of organic pollutants (Bonfatti et al. 1999; Borras et al. 2006). At the surface of these materials, water oxidation products, such as OH-, H2O2, O2 and O3, are generated indirectly by oxidizing organic pollutants. However, these anodes corrode and tend to become deactivated, diminishing their efficiency and useful life (Bonfatti et al. 1999). A previous work developed by Vlyssides et al. (1997) reports electrochemical incineration of vinasse in a cylindrical electrochemical reactor using a DSA as anode. Vinasse degradation was induced by active chlorine (given by the mixture of chlorine (Cl2), hypochlorous acid (HOCI) and hypochlorite ion (OCI-) ), electro-generated at the DSA in solution previously added with sodium chloride; this degradation is performed from an initial COD of 72000 ppm up to 8000 ppm. Partial vinasse degradation was due to the fact that active chlorine oxidants are weak oxidants. In addition to the above, the generation of chloroaromatic compounds following the electrotreatment makes the treated effluent be more toxic.

Synthetic boron-doped diamond electrodes (BDD), manufactured by chemical vapor deposition, have been recently used for organic compound degradation (Rodrigo et al. 2001; Zhi et al. 2003; Martínez-Huitle et al. 2004; Panizza et al. 2005; Butró n et al. 2007; Nava et al. 2007). H2O + BDD → BDD(OH·) + H+ + 1e– (1)

Recent reports carried out by our research group (Butró n et al. 2007 Nava et al. 2007) refer to electrochemical incineration of p and o-cresol, and dyes with 2-D BDD electrodes in a FM01-LC reactor, respectively; this reactor is a filter-press in which hydrodynamic flow enhances hydroxyl-organic contact at the BDD surface, a phenomenon that increases organic mineralization efficiency. However, no electrochemical incineration of vinasse with BDD electrodes has been performed in such cell. Moreover, even when it is well known that 3D electrodes improve space-time yield, such electrode configuration has not been used for electrochemical incineration purposes.

This manuscript considers electrochemical incineration of a synthetic vinasse solution which resembles an alcohol wastewater. Vinasse mineralization experiments in the FM01-LC reactor equipped with 3D BDD at constant current density, and variable hydrodynamics were performed.

**METHODS**

**Experimental details**

All solutions were prepared with analytical grade reagents and deionised water with 18 MΩ cm resistivity from a Milli-Q® system. Synthetic Vinasse solutions were prepared using 14.4 g L⁻¹ citric acid (20.1%), 11.2 g L⁻¹ glycerol (15.6%), 19.2 g L⁻¹ glucose (26.8%) and 26.88 g L⁻¹ sucrose (37.5%) giving a chemical oxygen demand (COD) of 75096 ppm; the resulting solution exhibits a conductivity of 2.5 mS cm⁻¹, and pH 3, maintained at 298 K. It is important to point out that the composition of the prepared solution resembles the vinasse originated from industrial production of alcohol wastewater.

**Equipment**

A potentiostat-galvanostat EG&G model PAR 273 and M270 software were used for all electrochemical experiments. Chemical oxygen demand (COD) analyses were performed using a dry-bath Lab Line Model 2008, and a
spectrophotometer Genesys 20. The cell potential was determined through an Agilent™ high impedance multimeter.

**Electrolyses in the FM01-LC**

As previously mentioned, the FM01-LC reactor has been described in detail in the literature (Brown *et al.* 1992; Griffiths *et al.* 2005; Butrón *et al.* 2007; Nava *et al.* 2007). An exploded view of the cell that includes the turbulence promoter used within the cell channel is shown in Figure 1. In this work the spacer was 0.6 cm thick. The electrodes were 3D BDD and a platinum coated titanium flat sheet, respectively. Details on the FM01-LC characteristics are given in Table 1. BDD electrodes were provided by Metakem™, with thickness of 2–7 μm supported on Ti expanded metal.

The undivided mode with a single electrolyte compartment and the electrolyte flow circuit for the FM01-LC cell is shown in Figure 2. The electrolyte was contained in a 1 L polycarbonate reservoir. A magnetic coupled pump of 1/15 hp March MFG, model MDX-MT-3, with a flow rate capacity up to 300 cm³ s⁻¹ was used; the flow rates were measured by a variable area glass rotameter from Cole Palmer, model F44500. The electrolyte circuit was constructed from Master Flex tubing, C-Flex 6424-16, 0.5 inch diameter, the valves and the three way connectors were made of PVC.

**Methodology for electrochemical incineration tests**

Electrochemical incinerations of synthetic vinasse were carried out in the FM01-LC cell at 10 mA cm⁻² current density, due to the fact that at such value the formation of BDD(OH⁻) takes place (Butrón *et al.* 2007; Nava *et al.* 2007). The electrolyses were performed at different Reynolds numbers, Equation (2), comprised between 22 ≤ Re ≤ 109.

\[
Re = \frac{ud_p}{(1-\varepsilon)\nu}
\]

where \(u\) is the mean lineer flow velocity of electrolyte in the channel of the FM01-LC, \(d_p\) is the particle size of the 3D BDD mesh, \(\varepsilon\) is the ratio of the free space in the channel to overall channel volume (overall voidage), and \(\nu\) is the kinematics viscosity. The incineration of organic matter was followed by COD analysis of samples taken at different times. The COD values were determined by closed reflux dichromate titration method (*Standard Methods for the Examination of Water and Wastewater* 1995).

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**Table 1 | BDD electrode dimensions, experimental details on the FM01-LC electrolyzer**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrode length, (L)</td>
<td>16 cm</td>
</tr>
<tr>
<td>Electrode height, (B)</td>
<td>4 cm</td>
</tr>
<tr>
<td>Electrode spacing, (S)</td>
<td>0.55 cm</td>
</tr>
<tr>
<td>Electrode area, 3D BDD (3 mesh), (A)</td>
<td>444 cm²</td>
</tr>
<tr>
<td>Particle size of the mesh, (d_p)</td>
<td>1.2 cm</td>
</tr>
<tr>
<td>Overall voidage, (\varepsilon)</td>
<td>0.62</td>
</tr>
<tr>
<td>Mean fluid velocity, (u)</td>
<td>from cm s⁻¹</td>
</tr>
<tr>
<td>Electrolyte volume within the FM01-LC</td>
<td>29.2 cm³</td>
</tr>
<tr>
<td>Electrolyte volume in the reservoir</td>
<td>1000 cm³</td>
</tr>
<tr>
<td>Kinematic viscosity, (\nu)</td>
<td>0.01 cm² s⁻¹</td>
</tr>
<tr>
<td>Temperature</td>
<td>298 K</td>
</tr>
</tbody>
</table>

Overall voidage is the ratio of free space in the channel to overall channel volume.

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**Figure 1 | Exploded view of the FM01-LC laboratory cell electrolyzer in the undivided mode (Griffiths *et al.* 2005).**
RESULTS AND DISCUSSION

Electrochemical incineration of vinasses in a FM01-LC using BDD electrodes

Figure 3 shows the decrease of the normalized COD for synthetic vinasse as a function of electrolysis time at different Re values comprised between $22 \leq \text{Re} \leq 109$, and at current density of $10 \text{ mA cm}^{-2}$. This current density was selected in order to maintain the electrode potential within the interval of $2.3 \text{ V} \leq E \leq 2.75 \text{ V vs. SHE}$, a range that favors the formation of OH radical (Butrón et al. 2007; Nava et al. 2007), the agent which induces vinasse oxidation. The analysis effectuated from Figure 3 demonstrates, on one hand, that with the progress of electrolysis, the normalized concentration of COD decreases. On the other hand, normalized COD depletion does not show marked improvement with the Re, at electrolysis time between $0 \leq t \leq 400 \text{ s}$; while at $t > 400 \text{ s}$, the incineration of organic matter slightly increases as a function of the Re number, indicated in the figure.

From the analysis of Figure 3, normalized COD depletion of organic matter at $t > 400 \text{ s}$, may be due to the fact that at high Re there is a better mass transport of the pollutants towards the anode surface where hydroxyl radicals are electrogenerated. However, the fact that rate of mineralization, at $0 \leq t \leq 400 \text{ s}$, does not show marked improvement with Re may be associated with the high concentration of organic matter and with a complex mechanism of vinasse degradation. It is important to point out that all of the electrolyses presented herein were developed in the undivided FM01-LC, for which reason the degradation of vinasse may also involve reactions at the cathode.

A kinetic analysis for the oxidation of vinasse was performed to evaluate the influence of hydrodynamic in its overall rate of oxidation. In Figure 4 are shown the values of global kinetic rate constant ($k$), obtained by linear
regression of the experimental data, using Figure 3 and Equation 3, as a function of Re. Equation (3) considers zero order kinetics, for the FM01-LC in recycle batch mode of operation (Figure 2), where the volume of electrolyte in the reservoir is 34 times greater than the contained within the FM01-LC, see Table 1.

\[
\frac{\text{COD}(t)}{\text{COD}(0)} = 1 - \left(\frac{k}{\text{COD}(0)}\right)^t
\]

From the analysis of Figure 4, it may be observed that the degradation kinetics of vinasse is slightly dependent on the Re. Moreover, the zero order kinetics indicates that the degradation is not completely controlled by mass transport.

The 97% mineralization of vinasse obtained herein (Figure 3), at Re of 109, was induced by the action of BDD(OH) produced on a BDD surface, which is in agreement to that reported with another pollutants on BDD electrodes (Rodrigo et al. 2001; Zhi et al. 2003; Martínez-Huitle et al. 2004; Panizza et al. 2005; Butró n et al. 2007; Nava et al. 2007). The achievement obtained in this paper is superior to that reported by Vlyssides et al. (1997), who obtained 89% mineralization in terms of COD, from and initial COD of 72000 ppm. Vlyssides et al. performed electrochemical incineration of such vinasse with titanium-platinum and stainless steel electrodes, with addition of sodium chloride. The low degree of mineralization reported by Vlyssides et al. is associated with the platinum material employed as anode, since platinum is a catalyst for active chlorine reaction, which is a weaker oxidant than OH-. On the other hand, it is important to remark that with the addition of chlorine simultaneous creation of chlorinated by-products/pollutants may produce a more hazardous effluent.

With the data obtained from COD for all of the electrolyses at their respective Reynolds values, integral current efficiency (\(\phi\)) was analyzed as a function of percentage of vinasse oxidation (Figure 5). The estimation of integral current efficiency was determined using Equation (4) (Butró n et al. 2007; Nava et al. 2007):

\[
\phi = \frac{4FV[\text{COD}(0) - \text{COD}(t)]}{It}
\]

where \(F\) is the Faraday constant (96,485 C mol\(^{-1}\)), \(V\) is the solution volume in cm\(^3\), \(\text{COD}(0)\) and \(\text{COD}(t)\) are the chemical oxygen demands at the beginning and at time \(t\) of the electrolysis in mol cm\(^{-3}\), \(I\) is the current applied in the electrolysis in ampere, \(t\) is the time of electrolysis in s, and 4 is the electron transferred of oxygen.

Figure 5 shows that current efficiency surpasses unity (maximum theoretical value) at all Re values studied. It important to observe that current efficiency, at the beginning of mineralization (% mineralization < 5) for all Re studied, is higher than that obtained for the subsequent mineralization (5 ≤ % mineralization ≤ 20). This last suggests that initial oxidation products formed by the interaction with BDD(OH\(^{-}\)) at the 3D BDD electrode enhance the degradation of the vinasse. HPLC studies would be helpful in the identification of possible vinasse oxidation products; however, these were beyond the scope of the present work.

On the other hand, current efficiency does not show marked improvement with Re, at 5 ≤ % mineralization ≤ 65 (Figure 5), indicating a complex mechanism of vinasse degradation as was previously discussed in Figure 3. However, at % mineralization ≥ 70, the increase of current efficiency as a function of Re, for Re ≥ 66, may be due to the fact that at high Re there is a better mass transport of the pollutants towards the anode surface.

It is important to mention that similar current efficiencies, surpassing unity, were obtained by Butró n et al. (2007) and Nava et al. (2007), during p and o-cresol and indigo mineralization process in the same FM01-LC reactor.
Nevertheless, these authors obtained lesser current efficiencies than the one presented herein. This latter can be due, on one hand, to the fact that the above mentioned authors used 2D BDD electrodes (with area = 64 cm²), unlike the present communication where 3D BDD electrodes (with area = 444 cm²) were employed. On the other hand, in this work the COD(0) of synthetic vinasse was 75.096 g L⁻¹, while Butrón et al. (2007) and Nava et al. (2007) work with dilute solutions with COD(0) < 1 g L⁻¹. Due to the above facts, high concentrations of COD and electrode area studied herein increase mineralization current efficiency in relation to the previously reported (Butrón et al. 2007; Nava et al. 2007).

Figure 6 illustrates the energy consumption by electrolysis ($E_c$) for the electrochemical incineration of vinasses performed at 10 mA cm⁻², as a function of the Reynolds number. Equation (5) was employed for the estimation of $E_c$ (Butrón et al. 2007; Nava et al. 2007):

$$E_c = \frac{4F E_{cell}V_m}{\phi V_m} \cdot \frac{1}{3.6}$$

where, $E_{cell}$ is the cell potential in V and $V_m$ is the molar volume in cm³ mol⁻¹. The value of 3.6 is a correction factor which converts $E_c$ to units of KWh m⁻³.

The analysis of Figure 6 shows that the energy consumption by electrolysis remains constant in a value ~ 245 KWh m⁻³ at Reynolds comprised between 22 ≤ Re ≤ 44; while at Re > 44, $E_c$ decreases to become constant in a value around 170 KWh m⁻³. The depletion of the energy consumption at 66 ≤ Re ≤ 109 suggests that such hydrodynamic conditions favor the electrochemical incineration of vinasse, due to the increase of current efficiency as was shown and discussed in Figure 5.

The experimental electrolysis achieved 97% efficiency at Re = 109 in vinasse mineralization and current efficiency that surpasses unity, indicating that the degradation of vinasse is better accomplished via hydroxyl radicals formed by the oxidation of water at the BDD surface, instead of active chlorine as usually occurs on platinum electrodes (Vlyssides et al. 1997). Estimated energy consumption, at Re = 109 and J = 10 mA cm⁻², was 168 KWh m⁻³. Experimental data revealed that vinasse degradation involves a complex mechanism.

CONCLUSION

Electrochemical incineration of a synthetic vinasse (COD of 75.096 g L⁻¹), performed in the FM01-LC, equipped with 3D BDD electrode, achieved up to 97% in vinasse mineralization with current efficiencies that surpass unity and energy consumption of 168 KWh m⁻³, at Re = 109 and current density of 10 mA cm⁻². The complete mineralization of vinasse indicates that such degradation occurs via hydroxyl radicals formed by the oxidation of water on the BDD surface. Experimental data revealed that hydrodynamic conditions slightly influence the vinasse degradation rate and current efficiency, indicating that the oxidation involves a complex pathway.

It is important to point out that electrochemical treatment proposed here could be adapted to a biotechnological treatment in order to reduce the cost of the treatment. On the other hand, it is important to mention that some partial degradation of vinasse lead them to be used as water for agricultural purposes. The above mentioned issues were beyond the capabilities of the present work; however, these analyses could be useful for vinasse treatment optimization.

ACKNOWLEDGEMENTS

The Authors acknowledge PROMEP project No. 33981 for the economic support. Janet C. Acosta thanks Mexican Sciences Academy (Summer Scientific Research Programme) for the grant given.
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