Electrochemical Treatment of Industrial Wastewater

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As the chemical industry commits itself to sustainable development, the importance of identifying alternative methods for wastewater treatment becomes more apparent. The removal or breakdown of organic compounds from wastewater is an important and integral part of any industrial chemical process. Described here is the electrochemical treatment (or pretreatment before biological treatment) of industrial wastewater (BASF wastewater) containing ter-butanol, a difficult biodegradable compound. Experiments were first carried out using model wastewater systems followed by industrial wastewater samples provided by a BASF Polymer Dispersion production plant in Ludwigshafen. The main results can be summarised in the following points:

a) Investigation of synthetic (or model) wastewater
   The electrochemical oxidation of ter-butanol at boron doped diamond (BDD) electrode is mass transport controlled. It can be achieved with a 100% current efficiency (in the absence of mass transport limitations). Other organics compounds present in the synthetic wastewater (e.g., acetone, methylacrylate, n-butanol) behave in a similar way. The current efficiency depends only on the chemical oxygen demand (COD) and it is independent of the nature of organic components present in wastewater.

b) Investigation of a BASF production plant wastewater sample
   Acetone and n-butanol are initially oxidised much faster than ter-butanol. However when they reach the ter-butanol concentration, all three components (acetone, n-butanol, ter-butanol) decay simultaneously with the same rate. It was found that by operating at the limiting current throughout the treatment process (monitoring the current density according to eq. (6)), the specific energy consumption for the electrochemical treatment can be strongly decreased to approximately 22 kWh/kg COD. During long-term electrolysis, electrode fouling by the formation of polymeric materials was observed.

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1. Introduction

The chemical industry's drive towards sustainable development has meant that research in wastewater treatment methods has increased in importance. Many industrial wastewaters also contain toxic organic compounds of which only some are biodegradable. Legal guidelines describe the wastewater requirements that have to be met by the user before it is discharged into the environment. Thus, several methods exist such as chemical oxidation\textsuperscript{(1-4)} (e.g., with O$_3$ and H$_2$O$_2$) and biological techniques. Hence, the industrial use of these treatments depends on their cost and their degradability efficiency.\textsuperscript{(5)} However, for those compounds, which are recalcitrant to the cited degradation methods, other technologies must be considered.

Recent research has demonstrated that electrochemistry is an attractive alternative to conventional methods for wastewater treatment since it does not involve the use of other chemicals.\textsuperscript{(6-12)} Several anode materials have been tested for the electrochemical oxidation of some organic model compounds. Recent studies demonstrated that the complete incineration of organics was possible using high oxygen overvoltage anodes.\textsuperscript{(13,14)} In fact, at a high overvoltage, electrogenerated hydroxyl radicals can degrade organic compounds to CO$_2$.

Since the discovery by Beer in the 1960s of the dimensionally stable anode (DSA),\textsuperscript{(15)} a great deal of interest was generated in the use of such electrodes in wastewater treatment. A further development of these electrodes was made by Gurevich and Pleskov\textsuperscript{(16)} in the form of boron doped diamond (BDD) electrode, which exhibits interesting electrochemical properties. BDD has a wide potential window for water stability and is stable in a highly concentrated acidic medium. Recently, this electrode has been successively applied in the field of electrochemical wastewater treatment.\textsuperscript{(17-20)}

The aim of this work is the elimination of ter-butanol (a compound not easily biodegraded) from industrial wastewater containing other easily biodegradable compounds. The composition of the BASF wastewater sample is given in Table 1.

In order to investigate the feasibility of the electrochemical treatment (or pretreatment before the biological treatment) of the BASF wastewater sample using BDD anodes, two series of experiments have been carried out:
- Experiments using pure products and model wastewater.
- Experiments with the BASF wastewater.

In both cases, results are compared with the predicted theoretical model developed in our laboratory.\textsuperscript{(17,18)}

<table>
<thead>
<tr>
<th></th>
<th>Concentration (ppm)</th>
<th>COD (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>742</td>
<td>1635.26</td>
</tr>
<tr>
<td>t-Butanol</td>
<td>310</td>
<td>803.02</td>
</tr>
<tr>
<td>Methylacrylate</td>
<td>407</td>
<td>680.78</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>475</td>
<td>1230.44</td>
</tr>
<tr>
<td>Others</td>
<td>–</td>
<td>136.04</td>
</tr>
</tbody>
</table>
2. Theoretical Model

A theoretical model that permits the prediction of the evolution of chemical oxygen demand (COD) and the instantaneous current efficiency (ICE) during the electrochemical oxidation of organic pollutants on BDD electrodes has been developed for an electrochemical reactor operating in a batch recirculation mode under galvanostatic conditions.\(^{17,18}\) The anodic oxidation of organic components has been assumed to be a fast reaction.

The formulation of the model starts from the estimation of the limiting current density from the COD values:

\[
J_{\text{lim}}(t) = 4Fk_m \text{COD}(t),
\]

where \(J_{\text{lim}}(t)\) is the limiting current density (Am\(^{-2}\)) at a given time, 4 is the number of the exchanged electrons, \(F\) is Faraday’s constant (Cmol\(^{-1}\)), and \(\text{COD}(t)\) is the chemical oxygen demand (mol O\(_2\) m\(^{-3}\)) at a given time.

Depending on the applied current density, two different regimes were identified (Table 2). When \(J_{\text{app}} < J_{\text{lim}}\) the electrolysis is under current control, the current efficiency is 100\% (eq. (2)) and COD decreases linearly with time (eq. (3)).

When \(J_{\text{app}} > J_{\text{lim}}\) the electrolysis is under mass-transport control, and secondary reactions (involved such as oxygen evolution) result in the decrease of the instantaneous current efficiency (eq. (4)). In this regime, the COD removal follows an exponential trend (eq. (5)).

The evolution of the limiting current density during the electrochemical treatment of given wastewater can be calculated from eqs. (1) and (5) (Table 2) with \(\alpha = 1\).

\[
J_{\text{lim}}(t) = 4Fk_m \text{COD}^0 \exp\left(-\frac{Ak_{\text{lim}}}{V_R} t\right)
\]

Table 2
ICE and COD trends for the two regimes. \(\text{COD}^0\) is the initial chemical oxygen demand, \(V_R\) is the reservoir volume, \(k_m\) is the mass transfer coefficient, \(A\) is the electrode area, \(\text{COD}^\alpha\) is the initial chemical oxygen demand, ICE is the instantaneous current efficiency, \(\alpha = \frac{J}{J_{\text{lim}}}\) and \(J_{\text{lim}}^0\) is the initial limiting current density.

<table>
<thead>
<tr>
<th>ICE</th>
<th>COD</th>
</tr>
</thead>
<tbody>
<tr>
<td>(J_{\text{app}} &lt; J_{\text{lim}})</td>
<td>(\text{ICE} = 1) (2)</td>
</tr>
<tr>
<td></td>
<td>(\text{COD} = \text{COD}^0\left[1 - \alpha \frac{A k_{\text{lim}}}{V_R}\right]) (3)</td>
</tr>
<tr>
<td>(J_{\text{app}} &gt; J_{\text{lim}})</td>
<td>(\text{ICE} = \exp\left(-\frac{A k_m}{V_R} \frac{1 - \alpha}{\alpha}\right)) (4)</td>
</tr>
<tr>
<td></td>
<td>(\text{COD} = \alpha \text{COD}^0 \exp\left(-\frac{A k_m}{V_R} \frac{1 - \alpha}{\alpha}\right)) (5)</td>
</tr>
</tbody>
</table>
3. Experimental

The boron doped diamond samples deposited on conductive p-Si substrates (p-Si/BDD) were provided by CSEM, Neuchâtel, Switzerland.

Oxidation of organics present in synthetic solution and in the BASF wastewater was performed in a one compartment electrolytic flow cell. Diamond was used as the anode and zirconium as the cathode, and both electrodes were discs (80 mm diameter) of 50 cm² geometric area with an interelectrode gap of 10 mm. The electrolyte was stored in a 500 mL thermostated glass tank and circulated through the electrolytic cell by means of a centrifugal pump. The flow rate of the electrolyte in the cell was 160 dm³h⁻¹ and the mass transfer coefficient (determined using the ferri/ferrocyanide couple) was 2×10⁻⁵ ms⁻¹.

The chemical oxygen demand (COD) was monitored during the electrolysis using a HACH DR2000 system. The total organic carbon was monitored using a Schimadzu TOC type 5050 during the experiment.

The instantaneous current efficiency (ICE) for the anodic oxidation of the organic compound was calculated using the following equation:

\[
ICE = \frac{4FV\left[(\text{COD})_t - (\text{COD})_{t+\Delta t}\right]}{I\Delta t}
\]

Here, (COD)_t and (COD)_{t+\Delta t} represent COD (mol O₂ m⁻³) at the time t and t+\Delta t respectively. F is the Faraday constant (C·mol⁻¹), V is the volume (m³) of the treated solution (wastewater) and I is the applied current (A).

4. Result and Discussion

4.1 Experiments using pure products

a) Electrochemical oxidation of ter-butanol

The oxidation of ter-butanol has been carried out in different electrolytes (H₂SO₄, HClO₄) under galvanostatic conditions. During electrolysis COD, TOC values have been measured and the ICE values have been calculated using eq. (7). The obtained COD and ICE trends have been compared with the theoretical values obtained using the model given in Table 2.

The experiments of the electrochemical oxidation of ter-butanol have been performed under a current density of 7 mA/cm², temperature of 30°C and with an initial concentration of ter-butanol of 203 ppm (COD=526 ppm) (Figs. 1 and 2).

The following observations were made:

- In region A (Figs. 1 and 2) ter-butanol is oxidised with a 100% current efficiency, yielding mainly carboxylic acids (oxalic, formic, acetic, etc.). At the end of this region A, ter-butanol is completely absent.
- In region B (Figs. 1 and 2) the intermediate oxidation products (oxalic, formic, acetic, etc.) are further oxidised with a low current efficiency yielding mainly carbon dioxide.

The fact that the theoretical model (see Table 2) is in good agreement with the experimental results (Figs. 1 and 2) clearly demonstrates that the electrochemical oxidation
Fig. 1. Electrochemical oxidation of ter-butanol in 1 M sulfuric acid. \( j = 7 \text{ mA/cm}^2 \), \( T = 30^\circ\text{C} \), initial concentration of ter-butanol = 203 ppm, (COD\textsuperscript{a} = 526 ppm). ● Experimental COD, ■ Experimental ICE, ▲ Experimental TOC. Continuous line: theoretical model (Table 2).

Fig. 2. Electrochemical oxidation of ter-butanol in 1 M perchloric acid. \( j = 7 \text{ mA/cm}^2 \), \( T = 30^\circ\text{C} \), initial concentration of ter-butanol = 203 ppm (COD\textsuperscript{a} = 526 ppm). ● Experimental COD, ■ Experimental ICE, ▲ Experimental TOC. Continuous line: theoretical model (Table 2).
of ter-butanol is a fast reaction and that under the investigated conditions, the reaction rate
is mass-transport controlled.

The global combustion reaction of ter-butanol on BDD is given by eq. (8).

\[ \text{C}_4\text{H}_{10}\text{O} + 7\text{H}_2\text{O} \rightarrow 4\text{CO}_2 + 24\text{H}^+ + 24\text{e}^- \] (8)

4.2 Experiments using synthetic wastewater

Synthetic wastewater in 0.1 M \( \text{H}_2\text{SO}_4 \) containing ter-butanol, methylacrylate, \( n \)-butanol
and acetone has been prepared (see Table 3 for the composition).

Electrolysis of this synthetic wastewater under galvanostatic conditions (\( j \approx 40 \text{ mA/cm}^2 \))
has been carried out at \( T = 30^\circ \text{C} \). During electrolysis, the COD and TOC have been monitored
and the instantaneous current efficiency ICE has been calculated from eq. (7). The obtained
results presented in Fig. 3 shows good agreement with the theoretical model given in Table 2.

<table>
<thead>
<tr>
<th></th>
<th>Concentration (ppm)</th>
<th>COD (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>700</td>
<td>1542.70</td>
</tr>
<tr>
<td>t-Butanol</td>
<td>300</td>
<td>777.11</td>
</tr>
<tr>
<td>Methylacrylate</td>
<td>450</td>
<td>752.70</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>500</td>
<td>1295.20</td>
</tr>
</tbody>
</table>

Table 3
Composition of synthetic (model) wastewater.

![Fig. 3](image-url)  
Fig. 3. Electrochemical oxidation of model wastewater in 0.1 M sulfuric acid. \( j = 40 \text{ mA/cm}^2 \),
\( T = 30^\circ \text{C} \). ● Experimental COD, ■ Experimental ICE, ▲ Experimental TOC. Continuous line:
theoretical model (Table 2).
This indicates that all the investigated organics are oxidised in fast electrochemical reactions and the process is mass-transfer controlled.

From these results we can conclude that:
- The electrochemical oxidation of tert-butanol is a fast reaction and the oxidation reaction rate is mass-transport controlled.
- The other organics present in the BASF wastewater (acetone, methylacrylate, n-butanol) behave in a similar way (fast electrochemical reaction and the oxidation reaction rate is mass-transport controlled).
- The current efficiency depends only on the chemical oxygen demand (COD) and it is independent of the nature of the organic compounds present in wastewater.
- It is possible to monitor the applied current density during electrolysis in order to achieve 100% current efficiency during all the processes.

4.3 Experiments using the BASF wastewater sample (Table 1)

The BASF wastewater contains a very fine white milky precipitate, which is difficult to separate even after centrifugation. The pH of the wastewater is 9.3 and the measured COD value is 12000 ppm. The composition of this wastewater is given in Table 1. The calculated COD from the composition given in Table 1 (4485 ppm) is much lower than the measured value (12000 ppm). This may be due to the presence of other unidentified products in the wastewater which aid in situ polymerisation reactions.

In order to increase the electrical conductivity of the wastewater, 0.1 mol/l Na₂SO₄ has been introduced followed by electrolysis under galvanostatic conditions (60 mA/cm²) at 30°C. The cell potential was 6.5 V and the obtained TOC and COD trends are given in Fig. 4.

Figure 4 shows that the rate of COD elimination during the electrochemical treatment is

![COD and TOC trends during electrolysis of BASF wastewater.](image)

Fig. 4. COD (theory and experiment) and TOC trends during electrolysis of BASF wastewater. $j = 60$ mA/cm², $T = 30°C$. Addition 0.1 M Na₂SO₄ in the wastewater.
3–4 times higher than the theoretical value. The main reason for this deviation is the fact that monomeric materials present in the wastewater are polymerised and a large amount of precipitate was observed on the electrodes and reactor walls. However, such polymerisation has not been observed in the case of the synthetic wastewater (Fig. 3). Other unidentified organic materials present in BASF wastewater may catalyse this polymerisation.

In the same experiment the main constituents of the wastewater (acetone, ter-butanol and n-butanol) have been monitored and the obtained results are given in Fig. 5.

This figure shows the presence of two regions: in region I acetone and n-butanol are oxidised at a faster rate compared to ter-butanol. However, when region II is reached, all three components of the system (acetone, n-butanol and ter-butanol) have almost the same concentration (almost the same COD) and decay simultaneously with the same rate. It is notable to mention that 85% of ter-butanol can be eliminated after the passage of a specific electrical charge of 9 Ah/l.

5. **Optimal Treatment Conditions and Electrical Cost Estimation**

For an efficient treatment of the wastewater, we propose to monitor the applied current using eq. (6) in such a way that we operate at the limiting current density during the entire treatment. In the case the instantaneous current efficiency is equal to unity (100%), the specific energy consumption ($E_{sp}$ in kWh/kg COD) can be calculated according to the following relation (eq. (9)).

$$E_{sp} = 3.35 \frac{V_0}{ICE}$$  \hspace{1cm} (9)

![Graph showing ppm vs. Q(Ah/l) for different chemicals: Acetone, ter-butanol, n-butanol.](image)

**Fig. 5.** Evolution of organic concentration during electrolysis of BASF wastewater. Conditions: idem Fig. 3.
Here, $V_e$ = cell potential (V), ICE = instantaneous current efficiency (0–1).

Considering that ICE = 1 (100% current efficiency) in the case of operation at the limiting current (eq. (6)) and $V_e = 6.5$ V, the specific energy consumption can be calculated as:

$$E_{sp} = 22 \text{ kWh/kg COD}.$$ 

6. Conclusions

The main conclusions of this work can be summarized in the following points:
- The electrochemical oxidation of the main organic compounds present in industrial wastewater (acetone, n-butanol, ter-butanol, methylacrylate) can be achieved with 100% current efficiency in the case of the absence of any mass-transport limitations.
- Extended periods of electrolysis result in the deposition of polymeric materials on the BDD anode surface. Work is now in progress in order to avoid polymerisation on the surface.
- The specific energy consumption in the absence of mass-transport limitations is approximately 22 kWh/kg COD.

References

19) S. Matsumoto and N. Setaka: Carbon 17 (1979) 485.