A new strategy for determination of current efficiency during electro-oxidation of aromatic compounds in a packed-bed system

Lizhang Wang, Yuemin Zhao, Qingyu Gao, Cheng Qian and Yunlong Hu

ABSTRACT

The electro-oxidation of aromatic compounds in 4,4′-diaminostilbene-2,2′-disulfonic (DSD) acid wastewater on IrO2-Ta2O5/Ti anodes was studied. The current efficiency was evaluated in terms of chemical oxygen demand (COD) by introducing a new factor, the fraction of the Faradaic current to the total cell current (β) through the network analysis of packed bed electrode system (PBEs). Experimental results using an up-flow PBEs at current intensities ranging from 5 to 16 A m⁻², flow rates ranging from 20 to 80 L h⁻¹ and inter-electrode distance of 5 to 50 cm are in good agreement with the proposed equation. In addition, lower current density, increasing flow rate and larger inter-electrode distance are beneficial to enhance the current efficiency.

Key words | aromatic compound, current efficiency, electro-oxidation, PBEs

INTRODUCTION

Current efficiency (η) is a key parameter associated with space-time yield, production conversion and energy consumption during electrochemical decomposition/synthesis. Until now, a chemical oxygen demand (COD) method proposed by Comninellis (Comninellis & Pulgarin 1991) is widely employed by researchers to describe the electrochemical treatment of wastewaters (Fockeley & Van Lierde 2002; Kong et al. 2007; Nageswara Rao et al. 2009). The calculation equation according to variation of COD between a given time t(s) and t + Δt is expressed as:

\[ η = \frac{(COD_t - COD_{t+Δt})FV}{8IΔt} × 100\% \]  

(1)

where COD_t and COD_{t+Δt} are the chemical oxygen demands at times t and t + Δt, F is the Faraday constant, V is the volume of electrolyte or effective volume of reactor and I is the applied current.

It deserves to be specially noted that Equation (1) is well suitable to the reaction in a parallel plate electrode reactor under constant volume and current condition. However, under galvanostatic condition with a continuous plug-flow operation, the changes of I and V with reaction time cause unavailable in obtaining constant values of these parameters. Furthermore, when the electrolysis is performed in a packed bed electrode system (PBEs), the calculated results of current efficiency by Equation (1) far exceed the theoretical value of 100% (Xiong & Karlsson 2002; Nava et al. 2008; Wang & Balasubramanian 2009). Therefore, we believe that there should be a rather different mechanism existed in PBEs from a parallel plate electrode one.

When charge is supplied to a packed bed, the bipolarity of filled particles causes the electro-oxidation occurrence both at the surface of anodes and particles, increasing the energy utilization. The enlargement of current efficiency is relevant to the current applied across the particulate electrodes, hence, a new parameter, the fraction of the Faradaic current of the microelectrodes to the total cell current (β) in PBEs, was introduced for the calculation of current efficiency in the proposed equation. Perhaps, it could be an explicit framework for understanding of what factors are involved in the synergistic work of metallic and particulate electrodes. Then, the experiments of kinds of current densities, flow rates and inter-electrode distances are conducted with continuous plug-flow conditions to examine the agreement between experimental and theoretical results.
using 4,4′-diaminostilbene-2,2′-disulfonic (DSD) acid wastewater, which contains aromatic compounds, such as 4-nitrotoluene-2-sulphonic acid and 4,4′-dinitro stilbene-2,2′-disulfonic acid, etc. At the same time, the reaction order also could be determined by the values of current efficiency: if the current efficiency always keeps constant value of 100%, the electro-oxidation would be zero order, i.e. at charge transfer control; while the first order reaction should be obtained when the current efficiency is continuously lower than 100% (Cossu et al. 1998; Deligiorgis et al. 2008; Panizza et al. 2008; Hmani et al. 2009). Hence, the development of the universal effective description of current efficiency of the overall electro-oxidations becomes a central problem before wide industrial application of the PBEs.

**EXPERIMENTAL**

The target solution was provided by Jingheng Chemical Co. Ltd (China) and it was obtained from reduction process of DSD acid manufacturing. The light green wastewater with pH 2.0–3.5 contained COD in the range of 500–700 mg L⁻¹ and sodium sulphate of 30–80 g L⁻¹.

The granular activated carbon (GAC) with a specific surface area of 680 m² g⁻¹ and an average particle size of 2.0–2.5 mm was washed several times with distilled water to remove the fines, oven-dried at 105 °C for 2 days to a constant weight prior to these experiments. A portion of weighted GAC was coated with cellulose acetate by soaking the carbon in cellulose acetate and the coated GAC was mixed with uncoated carbon in proportion as 1:1, avoiding short circuits between electrodes.

A quadrangular reactor with dimensions of 500 × 500 × 800 mm was constructed by polypropylene (PP). In this reactor, IrO₂-Ta₂O₅/Ti and Ti plates with active area of 0.25 m² (500 × 500 mm) were used as anode and cathode. Approximately 85.625 kg treated GAC was packed between anodes and cathodes up to a height of about 500 mm. A micropore plate was installed in the bottom of the reactor to support the weight of GAC and electrodes. Figure 1(a) shows the schematic representation of present experimental set-up. Wriggle pumps were used to pump the raw water into reactor. The power supply for the electro-oxidation was drawn from an electric motor (model: KZD2000/12) having capacity of 0–2,000 A/0–12 V. The constant temperature (25 ± 1 °C) for electrolysis was controlled with circulating water recycled from a temperature controlled water bath in the inlet and main body of the PBEs.

Kelvin bridge ohmmeter with type of 2,769 was used to measure by-pass resistance of the PBEs in order to calculate the value of β during electro-oxidation. The resulting solutions were filtered to remove any traces of GAC and then COD content was analyzed by APHA/AWWA/WEF (1998) for determination of current efficiency and reaction orders.

**MODELING**

Thank to their high contact resistance, easy repolarization and huge specific surface area, GAC particles act

![Figure 1](https://iwaponline.com/wst/article-pdf/63/11/2685/443669/2685.pdf)
as an ideal expanding electrode continuously and allow operation under relatively higher current density without any permeable diaphragm, causing the increase of space-time yields and different yield pathways of current. Therefore, from analysis by Figure 1(a) and (b), the total cell current at particulate electrodes partially plays roles in oxidation of organic compounds and the utilization is determined by Faradaic resistance ($r_2$) and by-pass resistance ($r_1$) with the expression of (King & Wright 1977):

$$\beta = \frac{r_1}{r_1 + r_2} \tag{2}$$

In Equation (2), the value of $\beta$ is only affected by kinds of electrode and filling materials, as well as configuration of the reactor and characteristics of wastewater. In this study, the measured $\beta$ values range from 0.88 to 0.90 with all operation conditions; therefore, the average value of 0.89 is used for the subsequent calculation. Hence, the mass balance for electro-oxidation under a given flow rate ($q$) could be obtained according to Faraday's law:

$$\eta = \frac{(1 + \beta) \int_0^\infty bidy}{nF} = q(c_0 - c_t) \tag{3}$$

where $c_0$ and $c_t$ are concentration of organics initially and at a given time $t$, $b$ is the width of electrodes, $i$ is the applied current density, $y$ and $y_0$ are diverse height of electrodes and bed height. From Figure 1(c), we can observe that the applied current is in linear proportion to bed height in a plug-flow operation and it can be easily calculated by the product of $b, y$ and $i$.

When the concentration is replaced by COD, Equation (3) is rearranged as:

$$\eta = \frac{Fq(COD_0 - COD_t)}{8(1 + \beta) \int_0^\infty bidy} \times 100\% \tag{4}$$

In principle, when the reaction is in charge transfer control, the current efficiency always keeps 100%, i.e.

$$\eta = 100\% \tag{5}$$

The duration of charge controlled regimes, i.e. the critical time between zero order and first order kinetics ($t_{Cr}$) could be obtained using heuristics by solving Equation (6)

$$\begin{cases} 
COD_{Cr} = COD_0 - \frac{8(1 + \beta) \int bidy}{Fq} \\
\tau_{Cr} = \frac{FqCOD_0 - COD_{Cr}}{8(1 + \beta)i} 
\end{cases} \tag{6}$$

where $x_0$ is the inter-electrode distance.

While at mass transfer controlled regime, the instantaneous current efficiency (ICE) should be given as:

$$ICE = \frac{8i}{Fk_mC_0} \tag{7}$$

and the current efficiency can be obtained from the integration of ICE during the electrolysis time necessary to reach a target COD ($r$) (Panizza et al. 2001):

$$\eta = \frac{\int_0^\tau ICE(t) dt}{\tau} \tag{8}$$

During this regime, the reaction is considered as first-order kinetics and written as (Polcaro et al. 2000; Anglada et al. 2009):

$$\frac{COD_t}{COD_0} = \exp(-kt) \tag{9}$$

then

$$\eta = \frac{8ikt_{Cr} - Fk_mC_0(C_0e^{-kt} - e^{-kt_{Cr}})}{8ikt} \tag{10}$$

where $k$ is the first order constant and $k_m$ is the mass transfer coefficient.

In addition, from Equation (4) we can also obtain the theoretical trends between COD and applied electrical quantity ($Q$) under the overall operation regimes.

$$\frac{COD_t}{COD_0} = 1 - \frac{8(1 + \beta)Q}{FVCOD_0} \eta \tag{11}$$

RESULTS AND DISCUSSION

Figure 2(a) depicts the normalized COD dependence of the electrical charge passed with different current densities. As can be seen from this figure, zero order (in charge control) and first order kinetics (in mass transfer control) are
perfectly reflected at 5 and 16 A m$^{-2}$, respectively. But operating at 12 A m$^{-2}$, the overall reaction should be simulated by initial zero order and subsequent first-order kinetics with the critical time of 2.26 h. Furthermore, the change of COD in charge control matches satisfactorily with the theoretical results obtained by Equation (11) at $\eta = 100\%$ (the dashed line). On the basis of analysis above, zero order kinetics leads to the current efficiency of 100%, the values of $\eta$ are determined by reaction constant regressed in Table 1 in mass transfer controlled regime and the current efficiency could be obtained using Equations (5) and (10) when the reaction is controlled by charge and mass transfer initially and finally. The agreement between theoretical curves and experimental results in Figure 2(b) further confirms these conclusions. This figure also shows that a lower current density easily leads to a completely utilization of the energy, while higher current density causes energy waste (Piya-areetham et al. 2006), which indicates that the increase of operation

![Figure 2](image-url)

**Figure 2** | Influence of applied current density (• 5 A m$^{-2}$; □ 12 A m$^{-2}$; ▲ 16 A m$^{-2}$) on variation of COD$_t$/COD$_0$ versus the specific electrical charge passed (a) and the current efficiency ($\eta$) versus reaction time (b) with flow rate of 10 L h$^{-1}$, inter-electrode distance of 10 cm and COD$_0 = 580$ mg L$^{-1}$. The solid lines represent the model predictions using Equations (5), (9) and (10) and the dashed line in (a) refers to theoretical results calculated by Equation (11) at current efficiency of 100%.

![Figure 3](image-url)

**Figure 3** | Influence of flow rate (• 80 L h$^{-1}$; □ 40 L h$^{-1}$; ▲ 20 L h$^{-1}$) on variation of COD$_t$/COD$_0$ versus the specific electrical charge passed (a) and the current efficiency ($\eta$) versus reaction time (b) with applied current density of 16 A m$^{-2}$, inter-electrode distance of 10 cm and COD$_0 = 580$ mg L$^{-1}$. The notations are the same as Figure 2.

Table 1 | Summary of zero and first order regression data for lab-scale rates of electro-chemical oxidation under different operation conditions

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Zero order</th>
<th>First order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k$ (h$^{-1}$)</td>
<td>$r^2$</td>
</tr>
<tr>
<td>$i = 5$ A m$^{-2}$</td>
<td>0.0797</td>
<td>0.9988</td>
</tr>
<tr>
<td>$i = 12$ A m$^{-2}$</td>
<td>0.1867$^a$</td>
<td>0.9994</td>
</tr>
<tr>
<td>$i = 16$ A m$^{-2}$</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>$q = 20$ L h$^{-1}$</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>$q = 40$ L h$^{-1}$</td>
<td>0.2471$^b$</td>
<td>0.9989</td>
</tr>
<tr>
<td>$q = 80$ L h$^{-1}$</td>
<td>0.2528</td>
<td>0.9999</td>
</tr>
<tr>
<td>$x_0 = 5$ cm</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>$x_0 = 10$ cm</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>$x_0 = 25$ cm</td>
<td>0.0969$^c$</td>
<td>0.9997</td>
</tr>
<tr>
<td>$x_0 = 50$ cm</td>
<td>0.0485$^d$</td>
<td>0.9995</td>
</tr>
</tbody>
</table>

$^{a,b,c,d}$The zero order kinetics ends at 2.26 h, 1.19 h, 1.76 h and 1.18 h, then the process starts by first order model with $k = 0.2426$ and $r^2 = 0.9939$, $k = 0.2928$ and $r^2 = 0.9996$, $k = 0.0507$ and $r^2 = 0.9999$ and $k = 0.1029$ and $r^2 = 0.9989$, respectively.
current density is not a better choice when energy consumption is taken into consideration.

The results (Figure 3) demonstrate that the current efficiency obviously increases with the increase of flow rate. When operating at a lower flow rate, a better COD removal can be obtained; however, the decrease of the current efficiency causes the process to be economically unviable (Solisio et al. 1999).

In Figure 4, it can be seen that the reduction of inter-electrode distance decreases the current efficiency sharply, but does better to COD removal. For example, at \( x_0 = 5 \text{ cm} \), the current efficiency is only 45% with COD removal of 88% (COD = 72 mg L\(^{-1}\)) in the outlet, which means the treated waste water can meet the need of discharge standard of 100 mg L\(^{-1}\) in China. However, when operating at \( x_0 = 50 \text{ cm} \), COD removal of 19% (COD = 472 mg L\(^{-1}\)) and current efficiency of 96% are obtained in the outlet, respectively. If the energy consumption is considered, the cost of the former would be at least 2 times of the latter.

Figures 2–4 illustrate the decrease of applied current density, increase of flow rate and reduction of the inter-electrode distance are beneficial to enhance the current efficiency, however, resulting in the lower COD removal. In addition, higher \( \eta \) values are observed at the earliest stage of these electro-oxidations. This is due to higher concentration of aromatic compounds in aqueous solution are available to capture and react (Deng & Englehardt 2007). As the oxidation proceeds, the continuous drop of \( \eta \) values can be explained by the fact that the mass transfer controlled process is easily arrived at low COD and the oxidation comes in competition with side reactions (e.g. oxygen evolution), causing the energy waste in the COD decay (Comninellis et al. 2008). Furthermore, the high agreement between experimental and theoretical estimation of \( \eta \) values in these figures also confirms that the introduction of \( \beta \) is very necessary to the accurate calculation of current efficiency in PBEs. As a result, another phenomenon should not be ignored: the experimental \( \eta \) values are higher than those of theoretical in all operating conditions; this is maybe because of the influence of measurement correctness of \( \beta \) values, further, the electrochemical generation of different kinds of powerful oxidizing agents also should be considered.

In the PBEs, the generation of peroxodisulfate (\( S_2O_8^{2-} \)) and \( \text{H}_2\text{O}_2 \) involved in the oxidation are as follows (Tatapudi & Fenton 1993; Alvarez-Gallbergos & Pletcher 1999; Lee et al. 2003; Cañizares et al. 2005):

\[
2\text{SO}_4^{2-} \rightarrow S_2\text{O}_8^{2-} + 2e^- \tag{12}
\]

acid condition: \( \text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O}_2 \tag{13} \)

alkaline condition: \( \text{O}_2 + \text{H}_2\text{O} + 2e^- \rightarrow \text{HO}_2^- + \text{OH}^- \)

\[
\text{HO}_2^- + \text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2\text{O}_2 + \text{OH}^- \tag{14}
\]

Regardless of these factors, the proposed Equation (4) for current efficiency in this study is in accordance with the experimental data. It could provide relatively satisfactory results for electrochemical oxidation of organic pollutants by a COD method when using PBEs.

**CONCLUSIONS**

Electro-oxidation of organic compounds in DSD wastewater with variation of current densities, flow rates and
inter-electrode distances were performed in a laboratory scale PBEs. The COD variation in the electro-oxidation is limited by charge transfer initially and mass transfer processes finally. The current efficiency was favored by the decrease of applied current density, increase of flow rate and reduction of the inter-electrode distance, but worsening the COD removal. In addition, the enhancement of current efficiency is for the increase of the interface reaction during the employment of GAC particles and the increment is relevant to the current applied across the particulate electrodes. Moreover, kinetics provided by introducing a new parameter, β, in this study matches experimental results of current efficiency satisfactorily in all operating conditions when using a continuous plug-flow operation. As a result, the present analysis confirms that employment of GAC as packing between anodes and cathodes can be a better candidate for enhancement of COD removal and current efficiency.

ACKNOWLEDGEMENTS

This research was supported jointly by the National Natural Science Foundation of China (Grant No. 50908226 and 50921002), Jiangsu Planned Projects for Postdoctoral Research Funds (Grant No. 1001022C) and the Youth Foundation of CUMT (Grant No. 2009A038).

REFERENCES


