Recent advances, challenges and prospects of in situ production of hydrogen peroxide for textile wastewater treatment in microbial fuel cells

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\textbf{INTRODUCTION}

Textile industries consume immense amounts of water and chemicals.\textsuperscript{1} Wastewater resulting from textile processes has impacts in terms of high COD, BOD, TOC, color, turbidity, temperature, wide-ranging pH (3 – 12), suspended solids and toxic organic compounds.\textsuperscript{2–4} Discharge of even a small quantity (ca. 1 mg L\textsuperscript{-1}) of dye is not acceptable and may produce toxic compounds at the end of the treatment process.\textsuperscript{5} It has been observed through market survey that the annual production of dyestuff is \textit{7} \times \textit{10}\textsuperscript{4} tons\textsuperscript{6–11} and approximately 10 – 15\% of the dyestuff is lost during the dyeing operation.\textsuperscript{12} Globally, almost 280,000 tons of textile dyestuffs are discharged into water sinks through textile effluents.\textsuperscript{13} For instance, in the textile cotton industry 0.6 – 0.8 kg NaCl, 30 – 60 g dyestuff, and 70 – 150 L water are required for dyeing 1 kg of cotton with reactive dyes. However, the wastewater produced contains 20 – 30\% of the applied unfixated reactive dyes with an average concentration of 2000 ppm and high salt content.\textsuperscript{14} This incurs economic glitches aside the environmental problems associated with waste discharge. Therefore, textile dying effluents require intricate treatment.\textsuperscript{15} Thus, a highly oxidative and non-selective oxidizing agent is needed for the treatment of textile wastewater.

In general, Advance Oxidation Processes (AOPs) such as ozonation, photocatalysis, sonolysis, electrochemical oxidation, Fenton and Fenton-like processes have the potential to produce highly oxidative and non-selective hydroxyl radical (HO\textsuperscript{•}).\textsuperscript{16} Compared with conventional methods, AOPs offer several particular advantages such as easy operation, high efficiency and less sludge formation.\textsuperscript{17} Among AOPs, the process that is gaining the attention of researchers and industry is Fenton process. This is because it can rapidly form HO\textsuperscript{•} radicals in acidic medium through interaction between iron salt and hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) (Equation (1)). The sequence of processes involved in the Fenton oxidation of textile wastewater is shown in Fig. 1.

\begin{equation}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{HO}^\bullet + \text{HO}^\bullet
\end{equation}

However, reaction parameters,\textsuperscript{18} type and excessive quantity of the iron salt used,\textsuperscript{19} high cost of H\textsubscript{2}O\textsubscript{2} and high chemicals requirement for pH modulation of real textile wastewater, are factors that hamper application of the Fenton process in textile wastewater treatment.\textsuperscript{20,21} Moreover, safety issues associated with the transport and handling of bulk quantities of commercially available H\textsubscript{2}O\textsubscript{2} and the energy intensive nature of the anthraquinone process\textsuperscript{22} make the process hazardous and uneconomical.\textsuperscript{22} This

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Figure 1. Sequence of processes for Fenton oxidation of textile wastewater treatment.

highlights the need to develop an in situ Fenton process, which is possible by in situ production of H₂O₂/HO• using AOPs. Among all AOPs, iron catalyzed processes²⁷–²⁹ require acidic conditions and end up with sludge formation. Ozone oxidation³⁰–³³ and photocatalysis³³–³⁷ are energy intensive. Photocatalysis is limited for small streams of wastewater and low dye concentrations while ozone relies on a high pH for HO• radical formation. However, the efficacy of these AOPs for H₂O₂/•OH radical production can be improved through sonolysis as an auxiliary tool, which is also highly energy intensive.³⁸,³⁹–⁴⁰ It is also evident from Table 1 that for almost all AOPs, operating costs make a significant contribution to the total cost of the process and thus make these processes highly expensive for wastewater treatment applications. Alternatively, smooth production of H₂O₂ via two electrons oxygen reduction reaction and continuous regeneration of Fe²⁺ from Fe³⁺ is possible with indirect electrochemical oxidation. Nonetheless, this process utilizes higher energy which hinders its application in textile wastewater treatment.⁴¹–⁴⁴ Also, the cost of electrodes contributes significantly to the total capital cost which can be estimated by the investigation in which the reported Boron doped diamond electrode costs of US$2.07E + 04.⁴⁵ Thus, the foregoing limitations associated with AOPs show the need to find and develop an alternative for in situ H₂O₂/•OH production that should be economical and energy efficient.

Scope of microbial fuel cells for hydrogen peroxide production

Wastewater based microbial fuel cells (WBMFCs) is sustainable technology⁴⁶ which is emerging as a substitute for electrochemical oxidation for in situ production of H₂O₂. It consists of anode and cathode compartments separated by a separator membrane. Substrate/organic matter in wastewater is oxidized by microbes in the anode compartment resulting in the formation of electrons and protons. Protons and electrons enter the cathode compartment through the separator membrane and the external circuit as shown in Fig. 2. Here, these are reduced by oxygen or some other electron acceptor to produce water (Equation (2)) or H₂O₂ (Equation (3)) through a four or two electron oxygen reduction reaction,⁴⁷ respectively.

\[
O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \quad (E^\circ = 0.816) \quad (2)
\]

\[
O_2 + 2e^- + 2H^+ \rightarrow H_2O_2 \quad (E^\circ = 0.295) \quad (3)
\]

Water synthesis following Equation (2) is commonly a recognized reaction with simultaneous power production. Over the last decade, the interest in generating power from wastewater treatment in WBMFCs has become a global quest with more and more researches emerging. The result obtained for a search with keyword ‘Microbial fuel cell’ from ‘Web of Science’ is presented in Fig. 3.

Interestingly, there has been almost 90% increase in papers published over the last decade while 3 and 16 published articles were found with keyword ‘In situ production of hydrogen peroxide in microbial fuel cells’ and ‘Production of hydrogen peroxide in microbial fuel cells’, respectively (Web of Knowledge, 2013). Two conclusions can be drawn from these results: (1) researchers have more interest in power production; and (2) the desired level for practical applications of power production in conventional WBMFCs is still not achieved.⁴⁸
Table 1. Estimated costs of AOPs

<table>
<thead>
<tr>
<th>AOPs</th>
<th>Capital cost ($/1000 gallons)</th>
<th>Operating and maintenance cost ($/1000 gallons)</th>
<th>Total cost ($/1000 gallons)</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fenton/US</td>
<td>1.59E + 08 (Roughly)</td>
<td>1.99E + 06 (without US)</td>
<td>1.61E + 08 (without US)</td>
<td>Emerging</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.35E + 06 (with US)</td>
<td>1.65E + 08 (with US)</td>
<td></td>
</tr>
<tr>
<td>Photocatalysis</td>
<td>2.67E +07</td>
<td>8.14E +07</td>
<td>8.36E +08</td>
<td>Emerging</td>
</tr>
<tr>
<td>Ozonation</td>
<td>4.53E +05</td>
<td>1.15E +05</td>
<td>5.68E +05</td>
<td>Emerging</td>
</tr>
<tr>
<td>US</td>
<td>8.23E +09</td>
<td>5.02E +08</td>
<td>8.73E +09</td>
<td>Emerging</td>
</tr>
<tr>
<td>US + O3</td>
<td>1.92E +09</td>
<td>5.28E +07</td>
<td>1.57E +09</td>
<td>Emerging</td>
</tr>
<tr>
<td>US + UV + O3</td>
<td>1.50e +09</td>
<td>4.43E +07</td>
<td>1.54E +09</td>
<td>Emerging</td>
</tr>
</tbody>
</table>

*Capacity = 1000 L min⁻¹

Figure 2. Hydrogen peroxide production mechanism in dual chamber WBMFC.

However, WBMFCs have the potential for in situ production of H₂O₂ not only for textile wastewater treatment but also for other recalcitrant contaminants as reported by Fu et al. The authors obtained 79 mg L⁻¹ of H₂O₂ at the pure graphite cathode using anaerobic sludge as an inoculum in dual chamber WBMFC. However, Modin and Fukushi obtained 2.3 g L⁻¹ of H₂O₂ at an energy cost of 8.3 kWh/kgH₂O₂ using municipal wastewater as an inoculum. It suggests that this technology has potential for H₂O₂ production at lower cost but it needs to be explored more for efficient wastewater treatment.

WBMFC has an edge over other methods as it offers several advantages for textile wastewater treatment. These include: (1) it is environment-friendly; (2) energy input is not required provided cathode chamber is aerated passively; (3) it does not evolve any off gas except CO₂ which is combustion free in nature; and (4) in situ production of H₂O₂ is cost saving.

Existing data on in situ production of H₂O₂ in WBMFCs especially for textile wastewater treatment is limited. Several factors including bacterial culture, type of anode and cathode used, electrode spacing, coulombic efficiency, power density, internal resistance, and configuration of WBMFCs must be studied in detail in order to solve the problems and challenges with in situ H₂O₂ production. Besides, bioelectrical current generated in WBMFC is directly linked with H₂O₂ production. Hence, the aim of this review is to highlight the potential of WBMFCs for in situ production of H₂O₂ for textile wastewater treatment with simultaneous power production. Moreover, it will also discusses in detail the recent advances in power production from wastewater treatment together with the weaknesses and strengths of WBMFCs.

Full text is available at: