Electrochemical Generation of Hydrogen Peroxide for Fenton Process for Glyphosate Herbicide Treatment

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Received 09 May 2017
Revised 19 October 2017; Accepted 28 December 2017

Abstract: One of the major and serious pollution issues in an agriculture-based country as Vietnam is derived from herbicide, especially Glyphosate herbicide which can cause a massive quantity of adverse effects and acute toxicity to aquatic life and human health. Hence, this research focused on setting up an electro-Fenton system with a Pt gauze anode and a commercial carbon felt cathode for Glyphosate herbicide treatment with the primary mechanism based on the in situ hydrogen peroxide electro-generation and ferrous ion catalyst regeneration. This study investigated effect of initial pH and current intensity on both the amount of hydrogen peroxide production and the Glyphosate mineralization performance. The results indicated that at pH 3, the quantity of \( \text{H}_2\text{O}_2 \) production on cathode was highest (~0.15 mg/L), and the Glyphosate mineralization performance was optimum, approximately 60% at an electrolysis time of 50 min. Moreover, when current intensity increased, the amount of \( \text{H}_2\text{O}_2 \) electro-generation increased, leading to a better Glyphosate mineralization efficiency. Nonetheless, in order to minimize the electrode corrosion as well as save energy cost, the optimum current intensity was found at 0.5 A.

Keywords: Electro-Fenton, hydroxyl radical, Glyphosate, hydrogen peroxide, herbicide removal.

1. Introduction

Glyphosate [N-(phosphonomethyl) glycine] is a broad-spectrum herbicide which has been widely used to kill unwanted plants both in agriculture and in nonagricultural landscapes. Glyphosate-containing products are acutely toxic to animals as well as humans, consequently causing a great deal of adverse effects including medium-term toxicity (salivary gland lesions), long-term toxicity (inflamed stomach linings), genetic damage (in human blood cells), effects on reproduction (reduced sperm counts in rats; increased frequency of abnormal sperm in rabbits), and carcinogenicity (increased frequency of liver tumors in male rats and thyroid cancer in female rats). Recently, the International Agency for Research on Cancer (IARC) of the World Health Organization (WHO) declared the herbicide glyphosate 'probably carcinogenic to humans (Group 2A) [1]. Therefore, many countries, such as Brazil, Argentina, Netherlands, Sri Lanka, Germany and Hungary were already on the road to eliminating the use of glyphosate. However, it is still liked and
widely-used in Vietnam, so people (mostly farmers) exposed to glyphosate herbicides can pose with an increased risk of miscarriages, premature birth, the cancer non-Hodgkin’s lymphoma as well as risks to aquatic ecosystems.

Therefore, the issue of removing pesticides in general, glyphosate in particular are becoming a big challenge in Vietnam. There are a large number of promising techniques for polluted water treatment such as membrane filtration, coagulation/flocculation [2] and biological methods [3–6], however, due to the glyphosate characteristics being refractory and difficult degradation, most traditional methods has met with several challenges, difficulties and inadequacies neither high cost, low efficiency nor secondary pollution issues. As an environmentally friendly electrochemical technology, electro-Fenton (EF) process is a promising method for degradation of refractory pollutants in general and glyphosate herbicide in particular in aquatic environment [7–8]. The EF process is based on the continuous in situ electro-generation of H₂O₂ (Eq. (1)) which is well-known as one of the most essential and versatile chemicals for pulp bleaching, waste treatment and numerous compounds manufacture [9–11], and it is promising for green chemistry and environmental control, especially for effluents treatment because it decomposes solely into water and oxygen, leaving no hazardous residues [12–14]. H₂O₂ can eliminate acquisition, shipment and storage, along with the addition of iron catalysts to produce powerful oxidant OH• (Eq. (2)) which can degrade most organic pollutants into CO₂, H₂O and inorganic ions under acidic conditions in a nonselective way. Therefore, the major concern with the EF system relates to the improvement of H₂O₂ production. In addition, the iron catalyst is produced continuously throughout the cathodic reduction of Fe³⁺ (Eq. (3)) [15].

\[ \text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O}_2 \]  \hspace{1cm} (1)
\[ \text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{OH}^+ + \text{OH}^- \]  \hspace{1cm} (2)
\[ \text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+} \]  \hspace{1cm} (3)

This paper represent a detailed discussion on Electro-generation of hydrogen peroxide for electro-Fenton using commercial graphite-felt which are widely used as cathodes due to the advantages such as no toxicity, good stability, high conductivity, and low catalytic activity of H₂O₂ decomposition. The effects of some operating parameters such as applied current and initial pH on the hydrogen peroxide production were also investigated.

2. Materials and methods

2.1. Materials

The carbon felt was purchased from A Johnson Matthey Co., Germany. Analytic grade glyphosate (C₃H₈NO₃P, Sigma Aldrich NY, USA) was used without further purification. Iron (II) sulphate heptahydrate (99.5%, Merck) and sodium sulphate (99%, Merck) were used as catalyst and supporting electrolyte, respectively. Sulphuric acid (98%, Merck) was used to adjust the pH of solution. Ninhydrin (C₉H₆O₄, Merck) and Sodium Molybdate (Na₂MoO₄, Merck) were used for spectrophotometric analysis of glyphosate. Potassium iodide (99%, Merck), potassium hydrogen phthalate (99.5%, Merck), sodium hydroxide (0.1N, Merck) and ammonium molybdate (99%, Fluka) were used in the hydrogen peroxide determination. All solutions were prepared with ultra-pure water obtained from a Millipore Milli-Q system with resistivity >18 MΩ.cm at room temperature.

Figure 1. Molecular structure of glyphosate.
2.2. Electro-Fenton system

The electro-Fenton system was set up with two electrodes in an undivided cylindrical glass cell of 7 cm diameter (capacity of 250 mL) at room temperature. The cathode was made of carbon felt with a specific surface area of about 60 cm$^2$ (12x5 cm in dimension), immersed in 200 mL aqueous solution containing a small quantity of glyphosate and ferric iron catalyst on the inner wall of the cell covering the totality of the internal perimeter. The anode was cylindrical Pt gauze (45 cm$^2$ area) placed on the centre of the cell and surrounded by the cathode (Fig.2). The distance between the electrodes was 1 cm. In order to supply O$_2$ for producing H$_2$O$_2$ from reaction, a compressed air was bubbled through the solutions at about 1 L.min$^{-1}$, starting 30 min before electrolysis. A small catalytic quantity of ferric ion was provided into the solution before the beginning of electrolysis. All solutions were vigorously stirred with a magnetic stirrer to allow mass transfer. The pH of solutions was adjusted by sulphuric acid. The electrical current was applied using a digital DC generator VSP4030 (B&K Precision, CA, US).

![Figure 2. Scheme of the electro-Fenton system: (1) Open undivided electrolytic cell containing the glyphosate solution, (2) carbon-felt cathode, (3) platinum anode, (4) magnetic stir bar, (5) digital DC generator.](image)

2.3. Instruments and analytical procedures

The pH was monitored using a Hanna HI 991001 pH-meter (Hanna instruments Canada Inc.).

The residual concentrations of glyphosate (before and after the treatment) were monitored by absorbance measurements using a GENESYS™ 10S UV-VIS spectrophotometer (Thermo Scientific Inc., USA). The method used to analysis glyphosate bases on the reaction of glyphosate with ninhydrin in presence of sodium molybdate in neutral aqueous medium to give a Ruhemann’s purple product having the VIS absorption maximum at 570 nm [16].

The concentration of accumulated H$_2$O$_2$ was determined spectrophotometrically by iodide method [17]. 0.75 ml of 0.1M potassium biphthalate and 0.75 ml of iodine reagent (0.4M KI, 0.06 M NaOH, ~10$^{-4}$M ammonium molybdate) were added to aliquots (1.5 ml) from the reactor, then the absorbance of the sample was measured with a GENESYS™ 10S UV-VIS spectrophotometer at $\lambda = 352$ nm ($\varepsilon_{I_2^-} = 26400$M$^{-1}$cm$^{-1}$).

The mineralization (conversion to CO$_2$, H$_2$O and inorganic ions) of glyphosate solutions was monitored from the decay of their total organic carbon (TOC), determined on a Shimadzu TOC-VCPh analyzer (Shimadzu Scientific Instruments, Kyoto, Japan). The percentage of TOC removal was then calculated from Eq. (4)

$$\%\text{TOC}_{\text{removal}} = \frac{\text{TOC}_i - \text{TOC}_t}{\text{TOC}_i} \times 100\%$$

(4)

Where TOC$_i$ and TOC$_t$ are the experimental TOC values at initial time and time $t$, respectively.

Total organic carbon (TOC) was measured during electrolysis using a Shimadzu TOC-VCPh analyzer (Shimadzu Scientific Instruments, Kyoto, Japan).
3. Results and discussions

3.1. Effect of initial pH on \( \text{H}_2\text{O}_2 \) electro-generation and mineralization performance

Effect of initial pH on \( \text{H}_2\text{O}_2 \) generation

The pH values play an important role in electro-Fenton process because it controls the quantity of hydroxyl radical production [18-21]. In order to investigate the impact of initial pH on the amount of \( \text{H}_2\text{O}_2 \) generation, the experiment was set up in an electro-Fenton system without both ferric catalyst and Glyphosate, with the applied current of 0.5A and the range of initial pH from 2 to 6. The results of \( \text{H}_2\text{O}_2 \) measurements at different electrolysis time were indicated in Fig. 3.

Fig. 3 illustrated that when the initial pH of solution reduce to acidic condition, from pH of 6 to 3, the quantity of \( \text{H}_2\text{O}_2 \) production on cathode increase continuously. Moreover, it is noticeable that the concentration of created \( \text{H}_2\text{O}_2 \) went up significantly during the first 40 min, then remaining stable. The reason can be when pH goes down, the \( \text{H}^+ \) concentration goes up leading to the number of generated \( \text{H}_2\text{O}_2 \) at cathode increases considerably due to the reduction process following the below reaction (Eq. 4):

\[
\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O}_2
\]

Nonetheless, when the pH values decrease continuously to lower than 3, the amount of generated \( \text{H}_2\text{O}_2 \) didn’t increase yet decrease gently. This phenomenon may be explained that with the too low pH values, the \( \text{H}^+ \) concentration is too high, consequently the reaction between \( \text{H}^+ \) and generated \( \text{H}_2\text{O}_2 \) might occur and create oxonium ion (\( \text{H}_3\text{O}_2^+ \)) (Eq. 5) and \( \text{H}_2 \) production reaction [22] (Eq. 6), causing the decrease in \( \text{H}_2\text{O}_2 \) concentration (Fig. 3).

\[
\begin{align*}
\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- & \rightarrow 2\text{H}_2\text{O} \quad (5) \\
2\text{H}^+ + 2e^- & \rightarrow \text{H}_2 \quad (6)
\end{align*}
\]

This result is matching with the research by Qiang et al, 2002 [23].

Effect of initial pH on Glyphosate mineralization

In order to investigate the effect of pH on Glyphosate mineralization efficiency by electro-Fenton, the electro-Fenton of 10^{-4} mol/L Glyphosate solution with the applied current of 0.1A, initial Fe^{2+} concentration of 10^{-4} mol/L and the pH value in range of 2 to 6.

As can be seen obviously from Fig. 4, the Glyphosate mineralization efficiency reached highest when the initial pH value of solution equals 3, approximately 60% at 50 electrolysis time. This result was corresponding to the above research output, the quantity of \( \text{H}_2\text{O}_2 \) generation was largest at the pH value of 3, then the amount of \( \text{OH}^- \) radicals were created significantly within this pH value. Moreover, this result can be effected by other factors, at pH larger than 3, Fe^{3+} may precipitate in form of Fe(OH)$_3$ amorphous, leading to reduce the amount of Fe$^{2+}$ catalyst and lower the Glyphosate mineralization performance. Otherwise, this hydroxide precipitation can cover electrodes surface inhibiting the Fe$^{2+}$ regeneration at cathode as well as blocking the electron exchange of some other electrolysis processes. Hence, it was rational to conclude that the pH of 3 can become the optimum pH value for \( \text{H}_2\text{O}_2 \) generation and Glyphosate mineralization by electro-Fenton.
3.2. Effect of current intensity on the quantity of H$_2$O$_2$ generation and mineralization performance

Effect of current intensity on the quantity of H$_2$O$_2$ generation

One of the most important factors influenced significantly on electro-Fenton performance because it affects to the amount of OH$^-$ radical production and these radicals become agents oxidizing organic compounds in solution [24]. To study the effect of current intensity on the amount of H$_2$O$_2$ electro-generation, the electro-Fenton process was carried out under the conditions: without Fe$^{2+}$ catalyst and Glyphosate, pH = 3 and different applied currents. The results of TOC analysis process were indicated in the following figure.

![Figure 5](image)

Figure 5. Effect of current intensity on the quantity of H$_2$O$_2$ generation during electro-Fenton process (pH = 3, V = 0.2 L, [Na$_2$SO$_4$] = 0.05M).

Fig. 5 illustrated that when the applied current increased, the number of H$_2$O$_2$ production also increased. The reason may be that the amount of electrolyte on the electrodes is directly proportional to the current intensity according to Faraday's law, so that the amount of H$_2$O$_2$ produced by the reaction (1) is directly proportional to the current intensity. Besides, when current intensity went up, the rate of Fe$^{2+}$ catalyst regeneration according to Eq. (3) also rose, consequently the amount of OH$^-$ radical creation and Glyphosate mineralization rate were in the same trend with current intensity (Ammar et al, 2015) [25]. This results is also corresponding to the research output by Dirany et al (2010) [26] and Panizza et al (2011) [27].

Effect of current intensity on Glyphosate mineralization performance

Effect of current intensity on Glyphosate mineralization rate by electro-Fenton process was investigated under conditions: 10$^{-4}$ mol/L Glyphosate solution, pH = 3, [Fe$^{2+}$] catalyst = 0.1 mM, current intensity in range of 0.1 to 0.5 A. The results of H$_2$O$_2$ determination were shown in Fig. 6.

It can be seen evidently from Fig. 6 that the TOC content reduced gradually by electrolysis time and the TOC decomposition rate increased when the applied currents went up from 0.1 to 0.5A. Since current intensity rose, the quantity of H$_2$O$_2$ increased due to the O$_2$ reduction process at cathode according to Eq. (1). It is reasonable that the H$_2$O$_2$ generation speed can be faster compared to Eq. (1) and the rate of Fe$^{2+}$ catalyst regeneration may be better compared to Eq. (3), leading to the larger amount of hydroxyl groups production from Fenton reaction. The results shown the same trend with the study performed by Dirany et al [26], Ting et al [28] and Oturan et al [29]. However, the use of high current intensity during electrolysis process can corrode electrode surface, causing decrease in electrode life-span. Therefore, applied current of 0.5 A could become the best choice for the following experiment.
4. Conclusion

The research on Electro-generation of hydrogen peroxide for electro-Fenton: Application in Glyphosate herbicide treatment shown that pH played a very important role in the amount of H₂O₂ generation on cathode as well as Glyphosate mineralization efficiency by electro-Fenton process. It was noticeable that with the pH value was 3, the quantity of H₂O₂ production on cathode reached largest, then the Glyphosate mineralization performance was optimum. Secondly, current intensity also influenced significantly on the number of H₂O₂ creation on cathode and Glyphosate mineralization rate. Specifically, when current intensity increased, the amount of H₂O₂ electro-generation increased, leading to better Glyphosate mineralization efficiency. Nonetheless, if electro-Fenton was carried out under high applied current causing fast electrode corrosion, then the optimum current intensity was 0.5 A.

Acknowledgements

This work was supported financially by the project of the Vietnam Academy of Science and Technology (VAST), under VAST07.03/15-16 project.

References


Sự tạo thành $\text{H}_2\text{O}_2$ trong quá trình fenton điện hóa để xử lý thuốc diệt cỏ Glyphosate

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Tóm tắt: Một trong những vấn đề ô nhiễm lớn và nghiêm trọng ở một nước nông nghiệp như Việt Nam là ô nhiễm thuốc diệt cỏ, đặc biệt là Glyphosate – chất có thể gây ra nhiều tác hại và độc tính cấp tính đối với sinh vật dưới nước và sức khỏe con người. Do đó, nghiên cứu này tập trung vào việc thiết lập một hệ thống Fenton điện hóa với điện cực ánốt làm bằng lưới Pt và catôt là vải carbon để xử lý thuốc diệt cỏ Glyphosate với cơ chế chính dựa trên việc tạo ra hydrogen peroxit tại chỗ và tái tạo chất xúc tác ion sắt. Ảnh hưởng của pH và cường độ dòng điện lên lượng $\text{H}_2\text{O}_2$ được sinh ra và hiệu quả khử hóa Glyphosate đã được nghiên cứu. Kết quả cho thấy tại giá trị pH = 3, lượng $\text{H}_2\text{O}_2$ được sinh ra trên catôt là lớn nhất, khoảng 0,15 mg/l, khi đó hiệu suất khử hóa Glyphosate là tối ưu, xấp xỉ 60% sau 50 phút điện phân. Mặt khác, khi cường độ dòng điện tăng lên thì lượng $\text{H}_2\text{O}_2$ được sinh ra cũng tăng lên, dẫn đến hiệu quả khử hóa Glyphosate tốt hơn. Tuy nhiên, để giảm thiểu sự ăn mòn điện cực cũng như tiết kiệm chi phí năng lượng, cường độ dòng điện sử dụng được giới hạn mở rộng 0,5 A.

Từ khóa: Fenton điện hóa, gốc hydroxyl, Glyphosate, hydroperoxit, loại bỏ thuốc diệt cỏ.