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ELECTRO-GENERATION OF HYDROGEN PEROXIDE: DERIVATION OF EMPIRICAL FORMULA SIMULTANEOUSLY CONTAINING CURRENT DENSITY AND ELECTROLYTIC TIME BASED ON KINETIC MODEL

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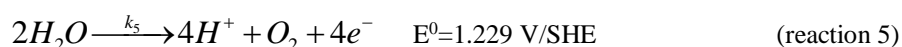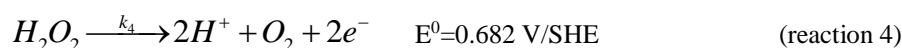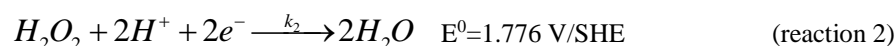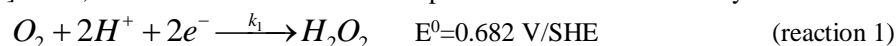
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Abstract

In this study an empirical formula based on kinetic model was established mathematically for describing electro-generation of H_2O_2. The kinetic model was derived by considering H_2O_2 generation and consumption simultaneously. The model was mainly related with two factors: current (I) and electrolytic time (t). Under a given current, the model of electro-generation of H_2O_2 only contains one factor (t). The experiment data verified this model, and we found H_2O_2 concentration is linear with the applied current at a current time. Based on this fact, an empirical formula was established mathematically for describing electro-generation of H_2O_2. The empirical formula of I/A and t, can predict the accumulative concentration of H_2O_2 ($[H_2O_2]$) at varied time, as well as at arbitrary current density within a certain range. It was deduced by the following two steps: obtain of linearity between $[H_2O_2]$ and I by theoretical assumption and experimental verification; obtain of exponential relationship between slope and intercept with t by curve fitting and reference to kinetic model. The related parameters of empirical formula were obtained through linear regression and curve fitting method. Finally, the value of H_2O_2 concentration predicted by the empirical formula fitted quite well with the measured one with difference less than 5%.

Introduction

As a kind of green chemicals, H_2O_2 has been widely used in a large number of applications, such as pulp and paper bleaching, water disinfection and reluctant organic pollutants degradation [1-5]. Hydrogen peroxide can be generated from two-electron reduction of oxygen as reaction (1) in an electrolytic cell[6]. In-situ electro-generation of H_2O_2 avoids hazards accompanying with its shipment and storage[7]. Hydrogen peroxide possesses characters of strong oxidation and liability which may lead gas release or runaway reactions[8]. With the electro-generated H_2O_2, added Fe^{2+} and acidic condition, electro-Fenton (E-Fenton) process can be realized [9-11]. E-Fenton process has been widely used to degrade recalcitrant organic pollutants in water [12-14]. During the electro-generation of H_2O_2, the H_2O_2 concentration is influenced by current density (or cathodic potential) and electrolytic time. To control the H_2O_2 concentration accurately in E-Fenton process, establishing the functional relationship between accumulated H_2O_2 concentration and electrolytic time is theoretically essential, and the relationship also can be used as instruction in E-Fenton process. The accumulative concentration of H_2O_2 during undivided electrolysis without Fe^{2+} and organics is the result of competition between its generation (reaction 1) and consumption (reaction 2, 3, 4)[6, 15-18]. Therefore the kinetic model of theoretical accumulative concentration of H_2O_2 can be mathematically derived through integration according to the principle of mass conservation. Liu[19] derived a kinetic formula which ignored the H_2O_2 consumption of anodic oxidation (reaction 4), as H_2O_2 was electro-generated in a divided "H-type" reactor and no consideration was given to anodic oxidation of H_2O_2. However, in an undivided reactor, H_2O electrolysis (reaction 5) occurs on a platinum (Pt) anode, on which H_2O_2 could be theoretically oxidized at the same time as the electrode potential of reaction 5 is much higher than that of reaction 4. More importantly, the existing kinetic model of H_2O_2 electro-generation can predict the accumulative concentration of H_2O_2 varying with electrolytic time just on the condition of one current density which is given already[20, 21]. However, the electrolytic reaction rate k_1, k_2 and k_4 are not constant which vary with potential (current density)[22, 23]. Thus, the kinetic model cannot make predictions under an arbitrary current density which is not given.

$$O_2 + 2H^+ + 2e^- \xrightarrow{\ k_1\ } H_2O_2 \qquad E^0 = 0.682 \text{ V/SHE} \qquad \text{(reaction 1)}$$

$$H_2O_2 + 2H^+ + 2e^- \xrightarrow{\ k_2\ } 2H_2O \qquad E^0 = 1.776 \text{ V/SHE} \qquad \text{(reaction 2)}$$

$$2H_2O_2 \xrightarrow{\ k_3\ } 2H_2O + O_2 \qquad\qquad\qquad\qquad \text{(reaction 3)}$$

$$H_2O_2 \xrightarrow{\ k_4\ } 2H^+ + O_2 + 2e^- \qquad E^0 = 0.682 \text{ V/SHE} \qquad \text{(reaction 4)}$$

$$2H_2O \xrightarrow{\ k_5\ } 4H^+ + O_2 + 4e^- \qquad E^0 = 1.229 \text{ V/SHE} \qquad \text{(reaction 5)}$$

To overcome the drawback of the kinetic model, we designed experiments of accumulative concentration of H_2O_2 varying with current density and electrolytic time simultaneously and developed an empirical formula through curve fitting statistically for

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accumulative concentration of H_2O_2 forecasting at arbitrary current density although it is not given yet. The empirical formula was based on the kinetic model which illustrated the tendency of H_2O_2 accumulative concentration functionally varied with electrolytic time, that the empirical formula should also follow.

In this study, we employed a carbon felt cathode which has a high specific surface and good conductivity to electro-generate H_2O_2[24-27]. The kinetic model of H_2O_2 electro-generation was established in consideration of all reactions of H_2O_2 generation and consumption. Then, the model was validated by the experimental data. Furthermore, an empirical formula containing two factors of current density and electrolytic time simultaneously was derived mathematically based on the linear regression analysis. The parameters of formula were calculated by fitting with the experimental data. Finally, the predicting value of H_2O_2 concentration through the empirical formula was verified with measured one.

Material & methods
Chemicals
Sodium sulfate (Na_2SO_4), hydrogen peroxide (H_2O_2, 30 *wt.* %) and sulfuric acid were purchased from Chuandong Chemical Inc., Chengdu, Sichuan, China. All reagents used in this work were analytical grade and used as received without further purification. All solutions were prepared with deionized water. The carbon felt (Taiwan carbon energy, Taizhong, Taiwan) cathode was cleaned with acetone under ultrasonic for 30 min, then washed with water and finally dried at 60°C for 4 h in an oven.

Instruments and procedures
The experiments for H_2O_2 electro-generation were conducted in an undivided glass vessel with volume of 0.2 L using three electrodes on CHI660D electrochemical workstation (CH Instruments, Chenhua, Shanghai, China). In the three-electrode system, the working electrode was the cleaned carbon felt disk (diameter 30 mm and thickness 3 mm); the counter electrode was a Pt plate (20 mm × 20 mm); the reference electrode was a saturated calomel electrode (SCE). The electrolyte was 150 mL 0.1 M Na_2SO_4 solution. As the electro-generated H_2O_2 would be used as Fenton reagent to degrade organic pollutants and the well-acknowledged optimal pH range for Fenton reaction is 2.0~4.0[28-30]. Thus the electrolyte pH in this study was adjusted to 3.0 using 1.0 M H_2SO_4 and 1.0 M NaOH monitored by a PHB-3 pH meter. Prior to electrolysis, air was bubbled near the working electrode at a flow rate of 100 mL min^{-1} for 10 min to saturate the aqueous solution. After the saturation of oxygen, H_2O_2 electro-generation electrolysis was performed at different current density for 120 min with a constant magnetic stirring of 400 rpm. The H_2O_2 concentration was determined by potassium titanium oxalate ($K_2Ti(C_2O_4)_3$) method (λ=405 nm) [31, 32] using a TU1810 UV-VIS spectrophotometer (Universal Analysis, Beijing, China). All the experiments were carried out at room temperature and repeated twice.

Results and conclusion
Kinetic modelling of H2O2 electro-generation and validation
Kinetic model establishing
It is generally believed that H_2O_2 electro-generation should involve the following four reactions: ① cathodic generation of H_2O_2 from dissolved oxygen reduction (reaction 1), ② further reduction of H_2O_2 on the cathode (reaction 2), ③ H_2O_2 disproportion in bulk regardless cell configuration (reaction 3) and ④ H_2O_2 oxidation on anode (reaction 4).

To establish a kinetic model for electro-generation of H_2O_2, we may assume that cathodic generation of H_2O_2 is directly proportional to the applied current density and the oxygen coverage on cathode surface. So the generation rate of H_2O_2 ($d[H_2O_2]/dt$) can be expressed by **Eq. (1)**:

$$\frac{\partial[H_2O_2]}{\partial t} = k_1 \frac{I\theta_{[O_2]}}{A} \tag{1}$$

Where I is the applied current, A is apparent surface area of the cathode, $\theta_{[O2]}$ is the oxygen coverage on cathode surface which can be expressed by the following equation, according to the Langmuir model, where K_{ad} is adsorption equilibrium constant[19]. In our experiments, as air was continuously bubbled into the electrolyte, $\theta_{[O2]}$ can be adopted as a constant.

$$\theta_{[O_2]} = \frac{K_{ad}[O_2]}{1 + K_{ad}[O_2]}$$

On the other hand, H_2O_2 decomposition rate depends on reaction 2、3 and 4. Reaction 2 represents the process that a fractional H_2O_2 are continuing to receive 2 electrons to form H_2O while reaction 3 stands for the dismutation reaction of H_2O_2. In terms of reaction 4, assuming that H_2O_2 decomposition on the anode is proportional to the applied current density and the concentration of H_2O_2 in the aqueous solution, according to the principle of mass conservation, the variation of H_2O_2 in unit time can be expressed by **Eq. (2)**:

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$$\frac{\partial [H_2O_2]}{\partial t} = k_1 \frac{I\theta_{[O_2]}}{A} - k_2[H_2O_2][H^+]^2 - k_3[H_2O_2] - k_4\frac{I[H_2O_2]}{A} \qquad (2)$$

According to the initial condition when $t=0$, $[H_2O_2]=0$, after integration, the $[H_2O_2]$ is a function of electrolytic time that can be expressed as **Eq. (3)**:

$$[H_2O_2] = \frac{k_1 I\theta_{[O_2]}}{Ak_2[H^+]^2 + Ak_3 + k_4I}[1 - e^{-(k_2[H^+]^2 + k_3 + \frac{k_4I}{A})t}] \qquad (3)$$

For **Eq. (3)**, when electrolytic time approaches infinity, $[H_2O_2]$ reaches its maximum value:

$$[H_2O_2]_{max} = \frac{k_1 I\theta_{[O_2]}}{Ak_2[H^+]^2 + Ak_3 + k_4I} \qquad (4)$$

Although the $[H_2O_2]$ is a function of electrolytic time and current density simultaneously, and the electrolytic reaction rate k_1, k_2 and k_4 are not constant which vary with current density [22, 23], $[H_2O_2]$ can be approximately regarded as a one-variable function of electrolytic time, once the current density is given. Thus, let $a=k_1I\theta_{[O2]}/(Ak_2[H^+]^2+Ak_3+k_4I)$, and $b=k_2[H^+]^2+k_3+k_4I/A$, **Eq. (3)** can be re-arranged in a simplified form as show below:

$$[H_2O_2] = a[1 - e^{-bt}] \qquad (5)$$

The parameters (a, b) of **Eq. (5)** which is consist with Liu's report[19] can be figured out through curve fitting method. And it can be concluded that **Eq. (3)** established as the kinetic model for H_2O_2 electro-generation can well describe H_2O_2 accumulation in aqueous solution against electrolytic time.

Validation of the kinetic model by experiments
Hydrogen peroxide electro-generation experiments with different current density (I/A) have been done to calculate the model parameters (a, b) and the obtained results were show in **Fig. 1**. It can be seen clearly that the kinetic model can well describe the accumulative H_2O_2 in aqueous solution varying with electrolytic time under different given current density. The fitting result also demonstrated that electrochemical reaction of H_2O_2 generation through oxygen reduction in acidic solution followed the exponential function model with five correlation coefficients of R^2=0.9997, 0.9994, 0.9999, 0.9999 and 0.9997. Thus, on condition that current density was given, fitting curve of H_2O_2 electro-synthesis could obtain to precisely predict the accumulative concentration of H_2O_2 in aqueous solution at arbitrary electrolytic time. Apparently, for any current density that is not given, the function of the accumulative concentration of H_2O_2 varying with electrolytic time cannot be fitted quantitatively.

Empirical formula inducing and verification
Empirical formula inducing
In order to make up for the drawback of kinetic model, an empirical formula for accumulative concentration of H_2O_2 forecasting at arbitrary current density was developed.

Curve fitting is a method of constructing a mathematical function that has the best fit to a series of data points [33, 34]. Experimental data were given by **Table 1** which shows the accumulative concentration of H_2O_2 varying with current density and electrolytic time simultaneously. It can be seen that the accumulative concentration of H_2O_2 increases with the current density raising under the range of 1.132~7.360 mA.cm^{-2}. However, when the current density reaches 9.342 mA.cm^{-2}, the accumulative concentration of H_2O_2 decreases instead. Therefor, 7.360 mA.cm^{-2} can be seen as the optimal current density in our experimental conditions. **Fig. 2**, where $t=120$ min, represents H_2O_2 concentration is linear with the applied current. Assuming that the functional relation between accumulative concentration of H_2O_2 and current density can be described as approximately direct proportion (**Eq. (1)** and dissolved oxygen in our experiments can be regarded as saturated in aqueous solution all the time) when the current density was less than 9.342 mA.cm^{-2}, the relationship between the accumulative concentration of H_2O_2 and current density can be expressed by **Eq. (6)**

$$[H_2O_2] = a' + b' * \frac{i}{A} \qquad (6)$$

Where a' and b' are functions of electrolytic time (t) as $[H_2O_2]$ is dependent both on i/A and t.

To validate **Eq. (6)**, five groups of experimental data within the optimal current density (1.132, 2.265, 3.963, 5.096 and 7.360, where 1.132 and 7.360 mA.cm^{-2} were required as two endpoints) were adopted to calculate the parameters of a' and b'. Another three were set as verification groups. The linear regression result was showed in **Fig. 3**.

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Fig. 3 demonstrates that accumulative concentration of H_2O_2 in aqueous solution is approximately proportional to current density at given time period with six correlation coefficients of R^2=0.9856, 0.9856, 0.9924, 0.9927 and 0.9914 under the current density of 1.132~7.360 mA.cm^{-2}.

As the intercept (*a'*) and slope (*b'*) vary with electrolytic time (*t*) which provides possibilities for establishing functional relationship between *[H₂O₂]* and *t*. In terms of the fitting trend, the functional relation between *a'*, *b'* and *t* can be expressed linearly, as well as exponentially (**Fig. 4**).

On one hand, the empirical formula should follow the kinetic model which illustrated the tendency of H_2O_2 accumulative concentration functionally varied with electrolytic time. And the fact that *[H₂O₂]* is an increasing function of *t* and the limiting value of *[H₂O₂]* will be constant as *t* approaches infinity which has been verified by the kinetic modeling and validating. On the other hand, considering the goodness of curve fitting (*R*-square), although the intercept, *a'*, can be represented by a linear trend (**Fig. 4, A-2**) as well as an exponential trend (**Fig. 4, A-1**), the trend of slope, *b'*, is better expressed by an exponential function than by a linear one. Thus, the electrochemical reaction of H_2O_2 generation followed the exponential function model (against *t*), the functional relation of *a'* and *b'* against *t* can be showed as follow:

$$a' = \alpha[1 - e^{-\gamma t}] \qquad\qquad (7)$$

$$b' = \lambda[1 - e^{-\kappa t}] \qquad\qquad (8)$$

Where α, γ, λ and κ are constants related with the physical and chemical properties of the cathode material.

Therefore, combined with **Eq. (6)**, *[H₂O₂]* varying with *i/A* and *t* can be further expressed by **Eq. (9)** (with the initial condition of *t*=0, *[H₂O₂]*=0)

$$[H_2O_2] = \alpha \frac{i}{A} * [1 - e^{-\gamma t}] + \lambda[1 - e^{-\kappa t}] \qquad\qquad (9)$$

Eq. (9) can be regarded as an empirical model for electro-generation of H_2O_2.

These parameters of α, γ, λ and κ could be figured out by curve fitting method. **Fig. 4** shows the exponential function relationship of *a'* and *b'* to *t* that can be expressed as follow:

$$a'=0.97971(1-e^{-0.0024567t}), R^2=0.9924 \qquad\qquad (10)$$

$$b'=0.72205(1-e^{-0.0100709t}), R^2=0.9998 \qquad\qquad (11)$$

After substitution of *a'* and *b'* into **Eq. (9)**, and with the initial condition of t_0=0, $[H_2O_2]_0$=0, *[H₂O₂]* can be eventually expressed as **Eq. (12)**

$$[H_2O_2] = 0.97971(1-e^{-0.0024567t}) + \frac{i}{A} 0.72205(1-e^{-0.0100709t}) \qquad\qquad (12)$$

Verification of empirical formula
In order to evaluate the accuracy of the empirical formula, three groups of measured data were contrasted with the predicted calculated from **Eq. (12)**. The result (**Fig. 5**) shows that the predicting value matches so well with the measured one that all the difference value between them are less than 5%. Thus, it can be regarded that the empirical formula successfully predicted the accumulative concentration of H_2O_2 from oxygen reduction in electrolytic cell. From the derivation process of the empirical formula, we know that the formula can apply to arbitrary current density within the range of 1.132~7.360 mA.cm^{-2} at any time for predicting the accumulative concentration of H_2O_2.

Conclusions
In this study, a conventional kinetic model of accumulative concentration of H_2O_2 electro-generated through oxygen reduction in electrolytic cell was established mathematically by considering both the H_2O_2 generation rate and consumption rate. Although the kinetic model includes two key factors of current density and electrolytic time simultaneously, the curve has to be fitted under given current density as the parameters are not constants which vary with current density. So the fitting curve can be only applied in prediction of accumulative concentration of H_2O_2 varying with electrolytic time under the given current density. An empirical formula was derived to be used as a feasible alternative for covering the shortage of the conventional kinetic model. The empirical formula can be applied to forecast the accumulative concentration of H_2O_2 at any time, as well as at arbitrary current density within a certain range. However, the restricted range of current density is the limitation of its application. Both the kinetic model and the empirical formula were only validated by the experiments of H_2O_2 electro-generation through carbon felt cathode. Further studies to apply the kinetic model and the empirical formula in other cathodic material become essential.
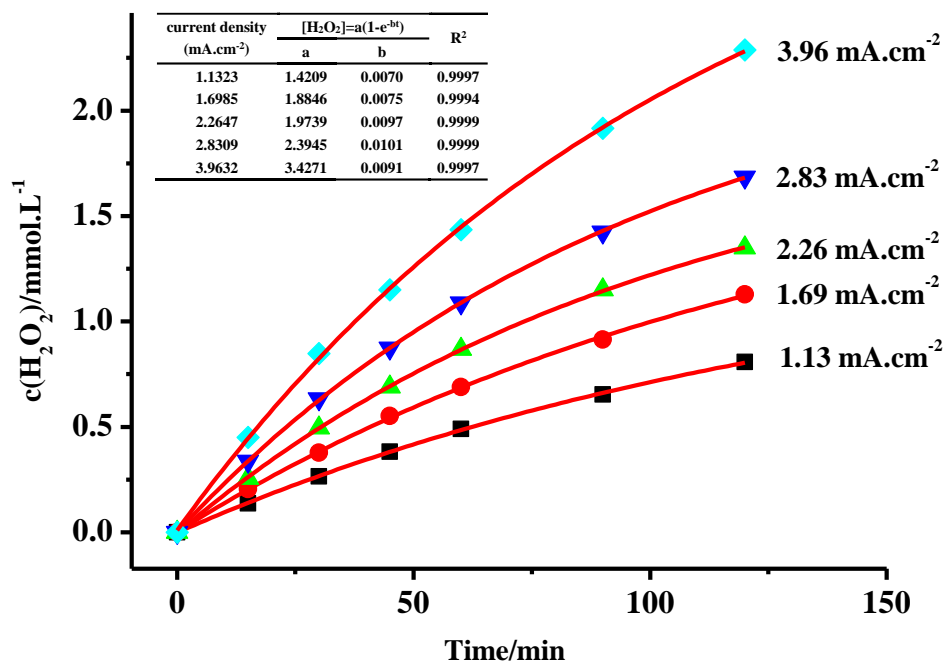
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current density (mA.cm^{-2})	[H$_2$O$_2$]=a(1-e^{-bt})		R^2
	a	b	
1.1323	1.4209	0.0070	0.9997
1.6985	1.8846	0.0075	0.9994
2.2647	1.9739	0.0097	0.9999
2.8309	2.3945	0.0101	0.9999
3.9632	3.4271	0.0091	0.9997

Fig. 1 Accumulative concentration of H$_2$O$_2$ in aqueous solution as a function of electrolytic time (0.1 M Na$_2$SO$_4$ as supporting electrolyte, pH$_0$=3.0, air flow rate: 100 mL min^{-1}, rotation rate: 400 rpm)

Table 1 Accumulative concentration of H$_2$O$_2$(mmol.L-1) varying with current density and electrolytic time

Current density (mA.cm^{-2})	Electrolytic time (min)						
	0	15	30	45	60	90	120
1.132	0	0.138	0.266	0.383	0.490	0.654	0.807
1.699	0	0.204	0.378	0.552	0.690	0.914	1.129
2.265	0	0.255	0.495	0.690	0.868	1.149	1.348
2.831	0	0.337	0.633	0.873	1.088	1.425	1.686
3.963	0	0.449	0.848	1.149	1.435	1.915	2.288
5.096	0	0.557	1.068	1.491	1.869	2.482	2.968
6.228	0	0.669	1.282	1.818	2.222	2.952	3.489
7.360	0	0.720	1.369	1.946	2.477	3.238	3.846
9.342	0	0.674	1.282	1.844	2.309	3.065	3.621

Experimental conditions: 0.1 M Na$_2$SO$_4$ as supporting electrolyte, pH$_0$=3.0, air flow rate: 100 mL.min^{-1}, rotation rate: 400 rpm

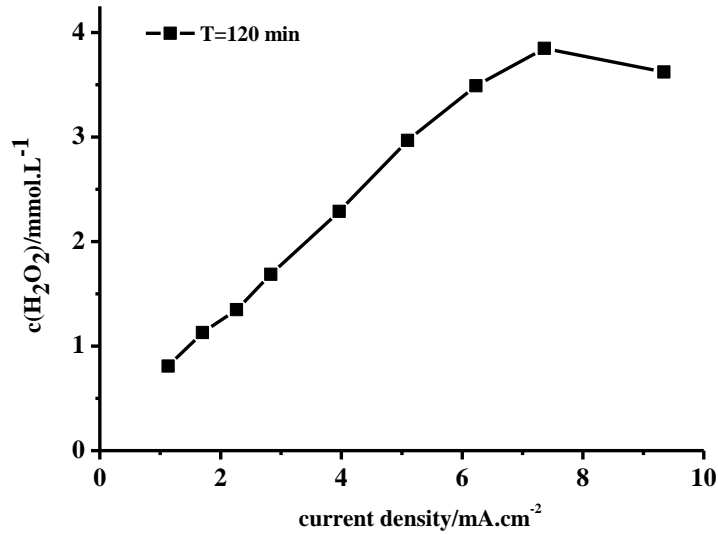Global Journal of Engineering Science and Research Management

Fig. 2 Accumulative concentration of H_2O_2 in aqueous solution varying with current density when t=120 min (0.1 M Na_2SO_4 as supporting electrolyte, pH$_0$=3.0, air flow rate: 100 mL.min^{-1}, rotation rate: 400 rpm)

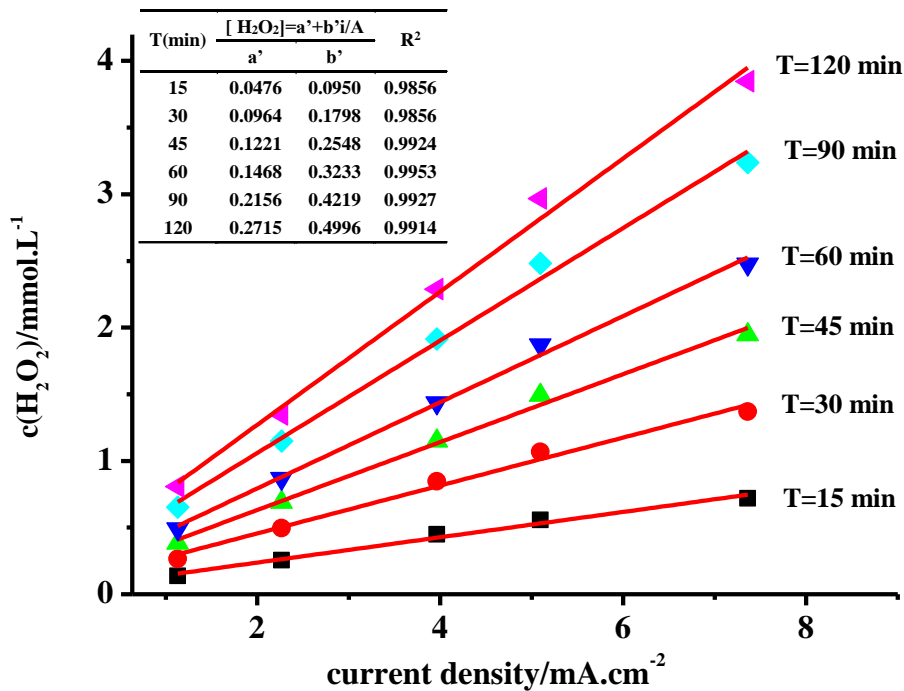| T(min)	[H_2O_2]=a'+b'i/A		R^2
	a'	b'	
15	0.0476	0.0950	0.9856
30	0.0964	0.1798	0.9856
45	0.1221	0.2548	0.9924
60	0.1468	0.3233	0.9953
90	0.2156	0.4219	0.9927
120	0.2715	0.4996	0.9914

Fig. 3 Accumulative concentration of H_2O_2 in aqueous solution varying with current density when t=15, 30, 45, 60, 90 and 120 min (0.1 M Na_2SO_4 as supporting electrolyte, pH$_0$=3.0, air flow rate: 100 mL.min^{-1}, rotation rate: 400 rpm)

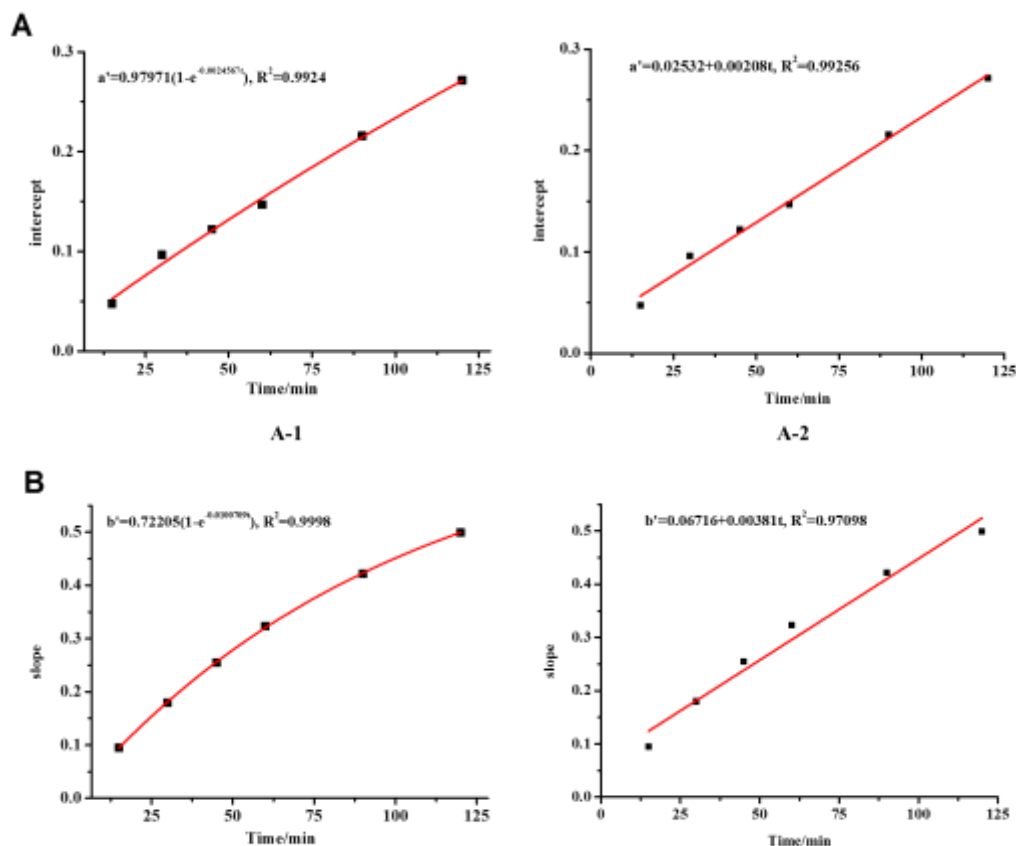## Global Journal of Engineering Science and Research Management

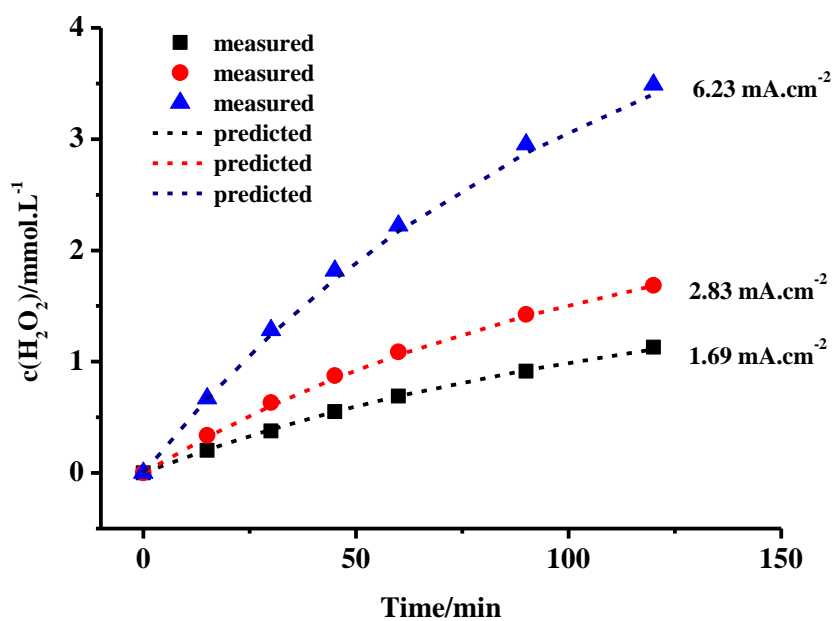**Fig. 4** Linear relationship of intercept (A) and slope (B) to electrolytic time.

Fig. 5 Verification of the empirical formula. (0.1 M Na_2SO_4 as supporting electrolyte, pH_0=3.0, air flow rate: 100 mL.min^{-1}, rotation rate: 400 rpm)

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