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Methods to improve electrochemical treatment effect of dye wastewater

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Abstract

Several methods, including changing electrolyte concentration, temperature, stirring, and voltage were studied to improve the degradation effect of electrochemical treatment in dye wastewater. In addition, nanophase TiO₂ catalyst and Co–Bi–PbO₂/Ti anode have been prepared to expedite color removal. Enhancement of temperature leads to proportional increase of color removal. As for voltage, at low levels its increase could greatly improves color removal. After voltage reaches about 3.0 V, its improvement effect declines quickly. The influence of electrolyte concentration and aerating on color removal are similar to that of voltage. So it favored to degrade organic pollutants using high salt concentration, high voltages and large electric current to improve treatment effect. However, the efficiency of energy supplied during electrolysis decreases. A nonlinear model is established to evaluate the influence of electrolyte concentration and voltage on color removal. The model agrees with the experiment data very well. It is suggested by the simulation result of this model that electrolysis degradation should better be carried out at about 3.0 V, in 0.01 M Na₂SO₄ concentration for high energy efficiency. Additionally, either catalyst or Co–Bi–PbO₂/Ti anode brings about 0.15 times more color removal without increasing electric current. Together, they could bring forth some 0.22 times higher color removal.

Keywords: Electrolysis; Dye; Wastewater treatment; Model; Electrolysis; C.I. Acid Red 14

1. Introduction

Since most textile wastewater has strong colors, highly fluctuating pH, high COD, bio-toxicity and large amount of suspended solids, there are problems to meet more stringent environmental regulations. Many methods have been conducted with respect to decolorizing these kinds of wastewater [1,2]. Because of its large variability of the composition, most traditional methods are becoming inadequate. Electrochemical technology and its application in wastewater treatment have been increasingly paid more attention to, because of its advantage of color removal [3].

According to traditional electrochemistry and recent study [5–7], electrolytic effect could be influenced by electrolyte concentration (conductivity), pH, temperature and electric voltage, etc. Addition of higher initial amounts of NaCl and HCl resulted in an improved removal of color and chemical oxygen demand (COD). Zhou et al. [7] have investigated electroctatalytic degradation of low concentration of phenol and its various affected

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0304-3894/\$ - see front matter © 2005 Elsevier B.V. All rights reserved. doi:10.1016/j.jhazmat.2005.09.010 factors such as current density, reaction temperature, and salinity of electrolyte. The addition of K_2SO_4 could lead to complete degradation of phenol. The result showed that treating phenolic wastewater is promising, with the addition of K_2SO_4 (1.0 g L⁻¹) at pH 5.6. The levels of salt concentration and acidity used for the treatment of wastewater containing organic pollutants by electrochemical method are markedly higher than that allowed by local legislations at the discharge point in rivers [6]. It is clear from the reported researches that most of the investigations favored to degrade organic pollutants using high salt concentration, high voltages and large electric current. Consequently, the efficiency of energy supplied during electrolysis decreased. So, it is necessary to set up an evaluation model to describe the influence of electrolyte concentration and voltage on electrolytic effect and find its optimal utilization parameters.

Anodic oxidation efficiency depends strongly on the electrode materials. As a whole, the anodes for organics oxidation should have high-overpotential for oxygen evolution. Otherwise, a great deal of current will be wasted to produce oxygen. In the past, graphite has been frequently used as an anode during electrochemical treatment, as it is relatively economical and gives satisfactory results. Recently, many investigations have been reported on the electrooxidation method using high-overpotential metal oxide anodes for oxygen evolution such as β-PbO₂/Ti, SnO₂/Ti and Pt/Ti or Pt-Pd/Ti electrodes [8-10]. PbO₂ and similar anodes have been considered to be of sufficient electro-catalytic oxidation for organic oxidation [11]. Most of these kinds of high O₂ evolution overpotential metal oxide anodes can bring about approving degradation effect. Feng and Johnson [12] developed Bi-PbO₂/Ti electrode to enhance its anodic oxygen-transfer capability. Iniesta et al. [13] studied using electrochemical method to treat biorefractory solution with high phenol content-1000 ppm, with Bi-doped lead dioxide electrodes, Bi-PbO2/Ti electrodes. Singh et al. [14] developed a kind of PbO2/Ti electrode doped with Co₃O₄ to strengthen its stability. To study the influence of electrode materials on anodic oxidation efficiency, graphite anode and a kind of high O₂ evolution overpotential metal oxide anode, Co-Bi-PbO₂/Ti anode, were used as electrodes, in this study.

However, the existence of catalyst in the electric field can also enhance the treatment efficiency [15-17]. In the electric field, many multivalence metal ions are added to expiate oxidation process [18]. Chen and Zhu [19] has used metal dioxide to treat three types of organic pollutants, i.e. phenol, phenylamine and di-Me phthalate from wastewater. The existence of H2O2 and •OH were verified during electrolytic catalytic process. The results showed that removal efficiency depended on the living intermediate yield in the system. Organic pollutants were effectively removed when H₂O₂ yield increased. Semiconductor catalyst can be used in electrochemical process as well as in photo-degradation reaction. Among the several methods proposed, photo-degradation catalyzed by suspended inorganic semiconductors (i.e. TiO₂) has lately received wide attention because it leads to non-toxic final products and show high degradation efficiency. TiO₂ is a semiconductor catalyst that has been widely studied since the 1970s. TiO₂ electrode has been used to degrade 4-chlorophenol and dyes [20,21]. Preparation and application of nanophase TiO₂ catalyst has been studied to enhance electrolysis efficiency in this research.

The mentioned influencing factors, electrolyte concentration, temperature, stirring, electric voltage, electrodes materials and catalysts, have great effect on electrolysis results. Thus, it is imperative to study these factors and to find how to operate electrochemical treatment more effectively. In this research Acid Red B (Acid Red 14, an azo dye) was used as model dye for electrochemical treatment.

2. Materials and methods

2.1. Electrolytic apparatus

Fig. 1 gives the scheme of electrolytic cell used in this study. There is a leading plank in the middle of the reactor. Air was pumped into through inlet at the bottom, below the leading plank. The stream of air flow and solution goes up along the leading plank in the right part of the electrolytic cell. After reaching the top of water level, solution goes down to bottom in the left part and moves circularly in the reactor. Catalyst was used as





Fig. 1. Schematic view of catalytic electrolytic cell.

powder suspended between the electrodes and flowing circularly with the solution. Electrodes, both graphite and Co–Bi–PbO₂/Ti anode, have an effective area of 40 cm².

2.2. Preparation of TiO₂ catalyst

Nanophase TiO₂ catalysts were produced using a proprietary sol–gel method. Tetrabutyl titanate and diethanolamine were dissolved in ethanol with a ratio of tetrabutyl titanate/ethanol = 1/11 by volume. After stirring for 2 h at room temperature, a mixed solution of 3% dilute HNO₃ and ethanol, HNO₃/ethanol 1.5/32 by volume was added to the precursor solution, with a magnetic burette under stirring, in a ratio of (mixed solution)/(tetrabutyl titanate/ethanol) = 1/3 by volume. So, the composition of the above solution included Ti (OC₄H₉)₄/C₂H₅OH/H₂O/HNO₃, 1/30/1/0.03 in molar ratio. The resultant alkoxide solution was kept at room temperature for about 10 h. Then it was heated at 400 °C for 3 h. All the chemicals used were analytic reagents. Prepared TiO₂ is ground to powder and was detected by an X-ray powder diffractometer (D8 advance, Bruker, German).

2.3. Preparation of Co-Bi-PbO₂/Ti anode

The Bi-PbO₂/Ti electrodes were obtained by the galvanostatic deposition in an acidic PbNO₃ solution according to the former work of Feng and Johnson [12]. Titanium plates $(5.0 \text{ cm} \times 8.0 \text{ cm}, 2.0 \text{ mm} \text{ thick})$ were cleaned with detergent water, and then immersed in 10% oxalic acid solution, boiling for 2-3 h. After cleaned with distilled water and dried in the air, they were dipped in 1 M HClO₄solution with 10 mM Pb(NO₃)₂, 7 mM Bi(NO₃)₂·5H₂O. Bi-PbO₂ Oxide film was electrodeposited at 1.8 V for 30 min. Later, the plate was washed with distilled water and dried with air. Then, Bi–PbO₂/Ti was doped with Co₃O₄ according to Singh et al. [14]. 100 mL of 0.15 M Co(NO₃)₂·5H₂O solution was sprayed to prepare Co₃O₄ film. The flow rate of solution was adjusted to $2.0-2.5 \text{ mL min}^{-1}$. Air was used as the carrier gas. In this spraying procedure, temperature above the plate surface was maintained at 400 ± 10 °C through an electronically controlled furnace.

2.4. Operation

Solution contained 60 mg L⁻¹ dye. Na₂SO₄ was used as an electrolyte and kept at 0.05 M except its influence is detected. As well, DC power supply was kept at 8 V, temperature at 25 °C, respectively, except testing their influence. TiO₂ was added to solution at 1.0 g L^{-1} in the solution, when its catalytic effect is tested. Electric current density was detected with the time course. Color was analyzed by U-3010 Spectrophotometer (Hitachi, Japan). The maximum absorbency visible wavelength was detected and used as color removal index. Color removal ratio was calculated as follows.

$$R \operatorname{color} \% = \frac{ABS_0^{515} - ABS^{515}}{ABS_0^{515}} \times 100\%$$
(1)

where in, ABS_{1}^{515} is the average value of absorbency at 515 nm. ABS_{1}^{515} is ABS value at 515 nm before electrolysis.

3. Results and discussions

When electrolysis runs, its voltages must exceed thermodynamic equilibrium potentials, because of the electrochemical polarization. Potential distribution of electrolysis reactor can be expressed by following equation.

$$V = \phi_{e,A} - \phi_{e,K} + |\Delta\phi_A| + |\Delta\phi_K| + IR_L + IR_A + IR_K \quad (2)$$

 $\phi_{e,A}$ and $\phi_{e,K}$ are equilibrium potential of anode and cathode, respectively. $|\Delta\phi_A|$ and $|\Delta\phi_K|$ are absolute value of anode overpotential and cathode overpotential, respectively. *I* is electric current. R_L is solution resistance. R_A and R_K are lead resistance to anode and to cathode, respectively.

Electric current, I, can be defined as two parts, I_{deg} and I_{gas} . I_{deg} represents the electric current to degrade organics, while I_{gas} represents that to breakup water and release gases.

$$I = I_{\rm deg} + I_{\rm gas} \tag{3}$$

So the color removal effect is proportional to I_{deg} other than to *I* in total. Many influencing factors, such as, electrolyte concentration, temperature, stirring and electric voltage have great effects on voltage distribution and current distribution.

3.1. Aerating

A stirring method, aerating has been tested to improve decoloration effect of electrolysis, while electrolytic current is kept at about 40 mA at various air rate. Electrolysis results at various air rates are given in Fig. 2. It is clear that aerating can improve degradation effect because it can enhance mass transfer and then weaken the electrochemical polarization of electrolysis process. So high air rate and drastic stirring lead to high color removal and high value of I_{deg}/I_{gas} . However, after air rate reach certain value, about 40 Lh^{-1} , its promotion effect becomes slight at higher air rate.

A typical UV–vis spectrum of Acid Red B before and after electrolysis at $100 L h^{-1}$ air rate is shown in Fig. 3. There is a maximum absorbency visible wavelength at 515 nm of dye Acid



Fig. 2. Electrolysis results at various air rates, 60 mg L^{-1} Acid Red B, 8 V, 25 $^\circ C$, 0.05 M Na₂SO₄, 40 mA, 40 min.

Red B. Also, there is an absorbency peak of ultraviolet near 320 nm. However, the two absorbency peaks decrease evidently after treatment. It can be concluded that the conjugated bonds of dye Acid Red B must be destroyed and the molecules are broken into small ones [22].

3.2. Electrolyte concentration

Adding salt into solution increases conductance and electric current of electrolysis. As shown in Fig. 4, the figure of conductance is almost an ascending straight line. However, the figure of electric current is a little winding. This lies in the alteration of voltage distribution between electrodes and in solution with uprising of salt concentration. When salt concentration is enhanced, solution resistance decreases and potential difference in solution decreases. Potential difference on electrodes, $|\Delta\phi_A|$ and $|\Delta\phi_k|$, increases. Hence, the higher the potential difference on electrode, the faster degradation of dyes.

Electrolytic results in various electrolyte concentrations at 8 V, 40 min are shown in Fig. 5. High salt concentration can improve the color removal effect. However, color removal is not proportional to the electric current and salt concentration. At low salt concentration, color removal is improved quickly with salt added in the solution. At high salt concentration, it increases slightly.



Fig. 3. UV–vis spectrum of 60 mg L^{-1} Acid Red B before and after electrolysis at $100 \text{ L} \text{ h}^{-1}$ air rate, 8 V, $25 \,^{\circ}\text{C}$, $0.05 \text{ M} \text{ Na}_2 \text{SO}_4$, 40 mA, 40 min.



Fig. 4. Conductance and electric current of various electrolyte concentration at 60 mg L^{-1} Acid Red B, 8 V, 25 °C, 40 min.



Fig. 5. Electrolysis results in various electrolyte concentrations at 60 mg L^{-1} Acid Red B, 8 V, 25 °C, 40 min.

3.3. Temperature

Most reaction rates are varied with temperature according to the convex-bent Arrhenius temperature dependence. High temperature increases the activity of molecules in solution. Consequently, electric conductance and electrolytic current will be increased with the enhancing of solution temperature. Electrolytic results at various temperatures are shown in Fig. 6. The



Fig. 6. Electrolysis results at various temperatures, 60 mg L^{-1} Acid Red B, 8 V, 0.05 M Na₂SO₄, 40 min.



Fig. 7. Electric current and conductance at various temperatures at 60 mg L^{-1} Acid Red B, 8 V, 0.05 M Na₂SO₄, 40 min.

color removal and electric current are roughly proportional to the temperature. So value of I_{deg}/I_{gas} must be steady with the increase of temperature. It is indicated that when temperature goes up, electric current rise. The proportion of electric current for degrading dye to that for side reactions keeps steady. That is, degradation of dye and evolution of oxygen are accelerated synchronously with temperature increasing (Fig. 7).

3.4. Voltage

Fig. 8 indicates that enhancement of electric voltage can improve the degradation effect. It is noted from voltage curve that at low voltages its increase greatly enhances the degradation effect. After voltage reach about 3 V, its improvement on color removal declines quickly. At high voltages most of current is consumed by oxygen evolution, side reactions. The electrochemical behavior of graphite anode has been characterized by previous work [22] that the oxidation current density and degrade potential have been evaluated. The oxidation potential is 0.9 V (versus SCE), i.e. 1.14 V versus Standard Hydrogen Electrode. The current density of Acid Red B is calculated as $1.0 \,\mathrm{mA}\,\mathrm{cm}^{-2}$ on a graphite anode. Hence, it is logical that after voltage reach about 3 V, the sum potential of $\phi_{e,A}$ and $|\Delta \phi_A|$ should exceed 1.14 V. As a result, its electrolysis degradation should be carried out at the voltages as 2-3 times high as the oxidation potential on the anode.



Fig. 8. Electric current and conductance at various voltages, $60\,mg\,L^{-1}$ Acid Red B, $0.05\,M$ Na_2SO_4, 25 $^\circ C$, 40 min.



Fig. 9. Comparison of three kinds of influencing factors, $60 \text{ mg } \text{L}^{-1}$ Acid Red B, 40 min.

As for these three kinds of influencing factors, electrolyte concentration, temperature and electric voltage, their effects are compared in Fig. 9. All of them can improve electric current and degradation effect. However, their utilization efficiencies of electric current are different. Slope rate of temperature is the biggest among three curves as a whole. Consequently, electric current increased by elevating temperature can lead to higher energy efficiency than by increasing voltages and salt concentration.

3.5. The effect of TiO_2 on color removal

Preparation and application of nanophase TiO_2 catalyst has been studied to expedite color removal. Fig. 10 shows a typical X-ray diffraction of nanophase TiO_2 catalyst prepared at 400 °C. TiO_2 prepared at this temperature is made of anatase structure. Using catalyst can bring about higher electrolytic efficiency at the same electrolytic voltage and electric current, as shown in



Fig. 11. Electrolytic results at various anodes and catalyst at 60 mg L^{-1} Acid Red B, 8 V, 40 mA, 25 °C, 0.05 M Na₂SO₄, 40 min.

Fig. 11. It leads to some 0.15 times higher color removal than without TiO_2 catalyst.

This is likely due to the fact that TiO_2 may be excitated to electron-hole pairs, e_{CB}^{-} and h_{VB}^{+} , by electric energy or by oxidant radicals in the solution, for it is proved TiO₂ as anodes can be excitated to electron-hole pairs by electric energy [20,21]. Kesselman et al. has used TiO₂ as a catalyst for the oxidative degradation of organic compounds in water. They used a potential source instead of light to generate reactive oxidants. It is demonstrated that polycrystalline TiO₂ particles electrochemically generates hydroxyl radicals at the TiO₂ surface. The valence band (h_{VB}⁺) potential is positive enough to generate hydroxyl radicals at the surface and the conduction band (e_{CB}) potential is negative enough to reduce molecular oxygen to hydrogen peroxide [23], which is continuously pumped into at the bottom of the reactor through inlet. The hydroxyl radical is a powerful oxidizing agent and attacks organic pollutants present at or near the surface of TiO2. It has been considered [24] that TiO₂ pre-adsorb organic compound at the particle/solution interface before degradation. Then oxidization happens directly



Fig. 10. Typical X-ray diffraction, $35 \text{ kV} \times 45 \text{ mA}$, of nanophase TiO₂ catalyst prepared at 400 °C.

or indirectly: (1) by direct oxidative transformation of the compounds that need to diffuse from the bulk solution to the semiconductor particle surface; (2) by oxidative radicals, such as $^{\circ}$ OH and $^{\circ}O_2$, generated from the oxidation of water and/or hydroxide ions by the valence band holes at the surface of semiconductor particles.

3.6. Anode materials

To detect the prepared Co–Bi–PbO₂/Ti anode, it has been tested to speedup removal of dye. PbO₂ and similar anodes are proved to oxidize organic pollutants effectively [11]. It must be due to the fact that it has high-overpotential for oxygen evolution. If else, a large amount of oxygen will be produced and lots of current supplied will be wasted, the degradation efficiency cannot be improved [25]. Co–Bi–PbO₂/Ti anode as a PbO₂ similar anode can bring about higher electrolysis efficiency, at the same electrolytic voltage and electric current, as shown in Fig. 11.

It is also revealed in Fig. 11 that either nanophase catalyst, TiO_2 or DSA, Co–Bi–PbO₂/Ti anode leads to some 0.15 times higher color removal than graphite anode. If this DSA anode and nanophase catalyst are used together to degrade dye, they could bring forth some 0.22 times higher color removal without increasing electric current. This catalytic method improves electrolysis effect without increasing electric current. Its application potential will be great if more effective catalysts or electrodes are invented.

3.7. Model development

The effects of the electrolyte concentration, voltage and electric current on the behavior of the degradation efficiency are different. It is postulated that organic pollutants could be oxidized directly by the anode or indirectly by O₃, H₂O₂, O₂, O₄, O₄, and other oxidants [1-4,20]. However, the relationship between oxidation of organic pollutants and current density has not been clarified. When electrolysis runs, there must be electron cavities on the anode, which leads to positive residual charge on the anode. So Organics could be oxidized directly on the anode. Kesselman et al. [20] have proved that there is electrochemical production of hydroxyl radical. Organics can be oxidized by both hydroxyl radical oxidation pathway and direct hole oxidation pathway. Certainly, the non-uniform concentration distribution in the applied voltage is shown to create a diffusion field causing the appearance of anodic current [26]. Organics must transport across the diffusion layer to the surface of electrode, and then is oxidized directly by electron cavity on the anode or indirectly by oxidants produced near the surface of anodes. Hence, the electric current and mass transfer in the near-electrode layer are relative to the applied voltages and electrolyte concentration.

The degradation process of organics can be described as Fig. 12. Organics near the surface are transported to the anode and then react with residual charge on the anode, or with O_3 , H_2O_2 , O_2 , $\bullet OH$, and other oxidants, forming intermediate RO. RO is soon broken into small molecular products, and then residual charge on the anode rejuvenates, or oxidants recruit quickly.

$$R + O \stackrel{k_{-1} \& k_1}{\longleftrightarrow} RO \stackrel{k_2}{\longrightarrow} R + P \tag{3}$$

R is residual charge intensity of electron cavities on the anode or oxidants produced near the surface of anode. *O* is organics concentration near the surface. RO is bonding intermediate. *P* is product of oxidation. K_1 is the diffusion rate constant of organics across the double layer. K_{-1} is the diffusion rate constant of intermediate RO off the anode. K_2 is the oxidation rate constant of intermediate RO into small molecular.

3.8. At various electrolyte concentration

The variation of RO concentration at various electrolyte concentrations must be as follows

$$\Delta \text{RO} = k_1([O] - [\text{RO}])[R] - k_{-1}[\text{RO}] - k_2[\text{RO}]$$
(4)

when the electrolysis keep steady, $\Delta RO = 0$, RO concentration can expressed as follows.

$$[\text{RO}] = \frac{k_1[O][R]}{k_1[R] + k_{-1} + k_2}$$
(5)

 I_{deg} representing the electric current to oxidize organics can be calculated as next equation

$$I_{\text{deg}} = nFk_2[\text{RO}] = nF\frac{k_2[O][R]}{[R] + k_{-1} + k_2/k_1} = I_{\text{max}}\frac{[R]}{[R] + k}$$
(6)

F is Faraday constant, approximately 96494 C, *n* electron number consumed by oxidizing one organic molecule.

Electric current is roughly proportional to electrolyte concentration as above Fig. 4. If residual charge intensity on the anode is suggested to be proportional to electric current, be relationship between color removal and electrolyte concentration can be expressed as follows.

$$R_{\text{color}} = R_{\max} \frac{[C]}{[C]+k} \tag{7}$$

3.9. At various voltages

Likewise, the variation of RO concentration at various voltages should be as follows

$$\Delta \text{RO} = k_1 ([R] - [\text{RO}])[O] - k_{-1}[\text{RO}] - k_2[\text{RO}]$$
(8)

when the electrolysis keep steady, $\Delta RO = 0$, SO concentration can be expressed as following Eq. (9)

$$[\text{RO}] = \frac{k_1[O][R]}{k_1[O] + k_{-1} + k_2}$$
(9)

 I_{deg} represents the electric current to oxidize organics must be as Eq. (10)

$$I_{\text{deg}} = nFk_2[\text{RO}] = nf \frac{k_2[O][R]}{[O] + k_{-1} + k_2/k_1} = I_{\text{max}} \frac{[O]}{[O] + k}$$
(10)



Fig. 12. Sketch map of oxidation mechanism of organics on the anode.



Fig. 13. Simulation results of relationship between color removal effect and electrolyte concentration.

At various voltages, transportation of organics to the surface is proportional to electric field intensity. So relationship between color removal and voltage can be expressed as follows.

$$R_{\text{colour}} = R_{\text{max}} \frac{V}{V+k} \tag{11}$$

Relationships between color removal and electrolyte concentration and voltage have been simulated according to Eqs. (7) and (11). The results are shown in Figs. 13 and 14, respectively. This model can match the experiment data very well. It is obviously shown from the simulation result that treating 60 mg L^{-1} Acid Red B at 8 V, 25 °C, and 40 min, color removal can get the highest value, about 35.07%, with enough electrolyte. Also treating 60 mg L⁻¹ Acid Red B with 0.05 M Na₂SO₄, at 25 °C, and



Fig. 14. Simulation results of relationship between color removal effect and voltage.

40 min color removal can get the highest value, about 29.89%, with enough high voltage. It can be concluded that electrolysis degradation had better be carried out at about 3 V, in 0.01 M Na_2SO_4 concentration to get high color removal and not consume too much energy.

4. Conclusions

Methods of changing electrolyte concentration, temperature, stirring, and voltage to improve degradation effect in dye wastewater electrolysis have been studied. Enhancement of temperature leads to proportional increase of color removal. Either Nanophase TiO₂ catalyst or Co-Bi-PbO₂/Ti anode brings about 0.15 times higher color removal. If this DSA anode and nanophase catalyst are used together to degrade dye, they could bring forth some 0.22 times higher color removal without increasing electric current. Aerating, adding salt, raising voltage can improve decoloration effect greatly at low value. Then their improvement becomes slightly at high value. A nonlinear model is set up to describe the influence of electrolyte concentration and voltage on color removal. The model matches the experiment data very well. The simulation result of this model suggests that electrolysis degradation should better be carried out at about 3.0 V, in 0.01 M Na₂SO₄ concentration to achieve high energy efficiency.

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