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Electro-Fenton degradation of cellulose using graphite/PTFE electrodes modified by 2-ethylanthraquinone

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1. Introduction

Cellulose is the most abundant and renewable organic substance in nature. To date, cellulose has mainly been utilized as a building material, or processed directly into paper or fiber. If cellulose can be efficiently converted to monomeric sugars, it can better compete with starch and play an important role to meet future energy needs. However the degradation of cellulose is limited because its chains have a strong tendency to aggregate to highly ordered structural entities due to their chemical constitution and spatial conformation (Zhao et al., 2007). It is well known that the degradation methods include acid degradation (Lin, Chang, & Hsu, 2009), thermal degradation (Kim, Eom, & Wada, 2010), biodegradation (Tilki, Yavuz, Karabacak, Çabuk, & Ulutürk, 2010), photocatalytic degradation (Malesic et al., 2005) and oxidative degradation (Lojewska, Miskowiec, Lojewski, & Proniewicz, 2005).

Among the new oxidation methods or advanced oxidation processes, electrochemical technologies are environment-friendly and effective for the direct production of hydroxyl radicals (•OH) via anodic oxidation or indirect generation via the electro-Fenton process. In recent years, the electro-Fenton methods have been studied widely to treat various organics in wastewater (Zhang, Yang, Gao, Fang, & Liu, 2008). This method is greatly effective because the oxidative potential of •OH formed in the medium reach

ABSTRACT

This paper reports an investigation on the degradation of cellulose via electro-Fenton method. The electrodes chosen were graphite/PTFE electrodes modified by 2-ethylanthraquinone (EAQ). The presence of EAQ greatly improved the rate of hydrogen peroxide formation on air-fed graphite/PTFE electrodes, which was determined by a UV spectroscopic method using molybdate as the color agent. Hydrogen peroxide can react with Fe²⁺ to form hydroxyl radicals in an acidic medium, which accelerates cellulose degradation by cleaving the glycosidic bonds between glucose units. The degradation products of the cellulose contain soluble sugar and 5-HMF, which were fully characterized by ¹H NMR and ¹³C NMR. © 2011 Elsevier Ltd. All rights reserved.

up to +2.8 mV, making the reactions between hydroxyl radicals and organic compounds take place much more easily.

In order to produce hydroxyl radicals (•OH), hydrogen peroxide must be present. Graphite flat plates (Leng et al., 2006; Qiang, Chang, & Huang, 2002), carbon felt electrodes (Ozcan, Sahin, Koparal, & Oturan, 2008; Pimentel, Oturan, Dezotti, & Oturan, 2008; Wei et al., 2007), three-dimensional electrodes made from reticulated vitreous carbon (RVC) (Alvarez-Gallegos & Pletcher, 1998; Gonzalez-Garcia, Banks, Sljukic, & Compton, 2007; Martinez & Bahena, 2009), and gas diffusion electrodes (GDE) (Brillas, Alcaide, & Cabot, 2002; Giomo et al., 2008; Panizza & Cerisola, 2008; Saha, Denggerile, Nishiki, Furuta, & Ohsaka, 2003) have all been used to reduce oxygen to hydrogen peroxide. Traditionally H₂O₂ is manufactured by the reduction of O₂ with H₂. The reaction is mediated by anthraquinone and demands high availability of hydrogen. Taking the traditional H_2O_2 manufacturing process as an example, we adopted a catalyzed H₂O₂ electro-generation process using modified graphite/polytetrafluoroethylene (PTFE) electrode, one of GDE, in which the catalyst had been incorporated into the graphitic mass. The organic catalyst chosen for the modification was 2ethylanthraguinone (EAQ) (Forti, Rocha, Lanza, & Bertazzoli, 2007). The H₂O₂ electrogeneration rate that was suitable for cellulose degradation was optimized relative to potential and catalyst concentration.

In this work, we adopted a UV spectroscopic method to determine if hydrogen peroxide was present using molybdate as the coloring agent. The present method is simple, rapid, accurate, and can be used for on-line process monitoring (Chai, Hou, Luo, & Zhu, 2004).

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2. Materials and methods

2.1. Materials

The following materials purchased from Tianjin Kermel Chemical Reagents Co. Ltd. were of AR grade: conductive graphite powder (99% purity), 60% polytetrafluoroethylene dispersion(PTFE), ethanol (99% purity), (NH₄)₆Mo₇O₂₄·4H₂O (99% purity), 3% hydrogen peroxide solution, 98% concentrated sulfuric acid, 37% chlorhydric acid, N,N-dimethylformamide (99% purity), CuSO₄ (99% purity), ethylenediamine (99% purity). 2-Ethylanthraquinone was supplied by Jilin Senxiang Chemical Products Distribution Co. Ltd. Cotton cellulose (Combed Cotton DP = 1100) was supplied by Hubei Xiangtai Co. Ltd.

2.2. MGDE preparation and behavior

Preliminary cyclic voltammetry experiments were performed to identify 2-ethylanthraquinone (EAQ) redox reactions in aprotic medium containing dimethylformamide (DMF) plus dried NaNO₃ 0.1 M (pH 7.0). For this, three electrode arrangement was used in the electrochemical cell with platinum foil serving as the working electrode, graphite electrode used as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. An electrochemical cell shown in Fig. 1 was used for the voltammetric and electrolysis experiments. Having been purged for 30 min by N₂ gas, the cyclic voltammogram was recorded in the aprotic medium with 20 mmol/L 2-ethylanthraquinone (EAQ) at 100 mV s⁻¹ potential scan rate. The scan range of potential was from -1.8 V to 0.5 V. All measurements were controlled by a TD-3691 potentiostat.

The modified gas diffusion electrodes (MGDE) precursor mass was prepared from conductive graphitic pigment, and a 60% polytetrafluoroethylene dispersion was used as hydrophobic binder. The weight ratio of conductive graphitic pigment to PTFE was 3/5. The mixture was homogenized in ethanol. Different contents of 2ethylanthraquinone, from 0 to 10% (wt.) relative to the graphitic carbon mass, were respectively incorporated into the MGDE precursor mass. They were heated at 80 °C until the precursor mass became ointment. They were then made into the cylinder (diameter 2 cm, thickness 0.5 cm) and dried at 110 °C for 24 h. MGDE was finally obtained after 1 h at 310 °C for calcination and solidification.



Fig. 1. Scheme of the electrochemical cell used in the voltammetric and electrolysis experiments.

The MGDE electrodes that were prepared with different concentrations of EAQ (0%, 0.5%, 1%, 3%, 5%, 7% and 10%) were selected as work electrodes. The reference was SEC and a graphite electrode was the counter electrode. The supporting electrolyte was 1 mol/L HCl and its pH value was about 1. The linear voltammetry was recorded from 0.2 V to 0.9 V vs. SEC at 10 mV s⁻¹.

Subsequently, controlled potential electrolysis was used for the optimization of H_2O_2 electrogeneration rate relative to the applied potential in the range of -2V < E < 0.4V vs. SEC. Experiments were performed with mechanical agitation. The air was insufflated into the cell through a pipe placed directly under the MGDE. The electrolyte was sampled after 30 min. Hydrogen peroxide concentration was determined by a UV–Vis spectrophotometer (TU-1810), recording the spectra from 200 to 500 nm. A solution of 2.4 mmol/L (NH₄)₆Mo₇O₂₄ ·4H₂O in 0.5 mol/L H₂SO₄ was added to the samples, which resulted in a yellow color. The absorbance was determined at 350 nm wavelength. Calibration plots based on Beer–Lambert's law were established relating absorbance to concentration (Chai et al., 2004).

2.3. Degradation of cellulose via electro-Fenton method

Potentiostatic electrolysis (-1.2 V vs. SEC) was conducted in an undivided cell shown in Fig. 1. The electrolyte was 1 mol/L HCl



Fig. 2. Overall reaction pathway for the oxygen reduction reaction mediated by EAQ redox catalyst and electro-Fenton reaction.



Fig. 3. Currents recorded for a line voltammetric potential scan on the MGDE surfaces with different EAQ concentrations.

100 mL plus 10 g cotton cellulose. In a new series of experiments, different weights of FeCl₂ (0g, 0.1g, 0.2g, 0.3g, 0.4g and 0.5g) were respectively added into this solution. The solution was then vigorously stirred with a magnetic bar. In order to reach a highly dissolved oxygen concentration for high H_2O_2 production, air was insufflated into the cell through a pipe placed right under the work electrode. The experiments were controlled by a potentiostat. The MGDE with 5% of EAQ was used as the work electrode. When the reaction was over, the residual cellulose and supernatant liquid were separated via filtration.

3. Results and discussion

3.1. MGDE behavior

A cyclic voltammogram was recorded on platinum foil for the aprotic solution containing 20 mmol/L of EAQ, in a potential range from 0.5 V to -1.8 V vs. SEC. Two pairs of reversible peaks are clearly observed. These peaks are relative to the EAQ reduction in two steps separated by almost 0.5 V. Such a potential separation may result in an intermediate compound, a quinone radical, as already hypothesised in the literature (Tammeveski, Kontturi, Nichols, Potter, & Schiffrin, 2001). Since a short-lived quinone radical is highly reactive, the EAQ redox cycle involved in the oxygen reduction may include the radical compound instead of the EAQ itself (Forti et al., 2007) as shown in Fig. 2.

The MGDE electrodes, prepared with different concentrations of EAQ, were used for the synthesis of hydrogen peroxide in the aqueous medium (1 mol/L HCl, pH 1). Currents of EAQ electrode recorded in these experiments were proportional to EAQ concentration. Fig. 3 shows a linear voltammetric potential scan for the MGDE. Current values recorded in these experiments were likely a result of two simultaneous processes: direct reduction of oxygen on the graphite surface, and reduction of EAQ. When the catalyst (EAQ) concentration was increased, an increasing current response was observed as a consequence of reduction of the overpotential for the formation of hydrogen peroxide.

As can be seen from Fig. 3, when increasing the amount of 2-ethylanthraquinone from 0 to 5%, the reduction peak potential decreased and the reduction peak current increased gradually. As the dosage of 2-ethylanthraquinone increased to 7%, no significant variation in the peak potential and current was observed. For the MGDE containing 5% EAQ, the maximum potential values of the



Fig. 4. XRD patterns of cellulose before (A) and after (B) degradation with electro-Fenton method.

reduction and oxidation peaks were corresponding to 500 mV and 780 mV, making the potential of this reaction 640 mV. It is known that the standard potential of oxygen direct reduction to hydrogen peroxide in the acidic solution is 0.68 V. Therefore, the redox peak of Fig. 3 must have been caused by oxygen direct reduction to hydrogen peroxide.

Two different electrodes with 0% and 5% EAQ were contrastively used for the synthesis of hydrogen peroxide under the same experimental conditions mentioned above. The largest amount of H_2O_2 production was 23 mg/L when using 5% MGDE with the potential being -1.2 V vs. SEC, although the produced hydrogen peroxide concentrations with the two electrodes gave similar rising profiles from 0.4 V to -1.2 V vs. SEC. More negative potential values would stimulate water production in a four-electron reaction.

In electro-Fenton methods, •OH radicals are produced from Fenton's reaction between hydrogen peroxide (H_2O_2) generated from two-electron reduction of oxygen at the cathode and Fe²⁺ present in the medium. We will research the effect of hydroxyl radicals on the degradation of the cellulose.

3.2. Degradation of the cellulose via electro-Fenton method

The MGDE with 5% EAQ was used for degradation of the cellulose. The profiles of the FTIR spectra were very similar before and after degradation of the cellulose, whereas the intensity of the peaks differed slightly. The crystalline allomorphs of cellulose were determined by the resolution of wide-angle X-ray diffraction measurement (Philips PW3040/00 X'Pert MPD instrument, the diffracted intensity of Cu K α radiation k = 0.1542 nm; 50 kV and 40 mA). The X-ray diffractograms in Fig. 4 shows the crystallinity of cotton cellulose sample (A) and the partly depolymerized cotton cellulose (B). Compared Fig. 4A, Fig. 4B is indicative of a low crystalline, low intensity peaks at 2θ = 22.8°. In addition, the total degree of crystallinity is 22,452 in Fig. 4A and 15,272 in Fig. 4B at 2θ = 22.8°, according to the Gusev method (Gusev, 1978). This can be seen as a dramatic decrease in crystallinity of the partly depolymerized cotton cellulose with electrocatalytic depolymerization.

The average degree of polymerization (DP) of cellulose was determined via copper ethylenediamine (CED) solution method (ISO5351/1). Having electrolysed for 1 h in 1 mol/L HCl electrolyte with MGDE of 5% EAQ, the DP of the cellulose decreased from 1100 to 706 due to the acid degradation. Furthermore, the DP of cellulose decreased to 390 when adding 0.2 g FeCl₂. An amount of hydrogen peroxide synthesized by MGDE reacted with Fe²⁺ to



Fig. 5. Suggested mechanism of degradation of the cellulose by hydroxyl radical-catalyzed.

produce hydroxyl radical which might accelerate the degradation of cellulose.

When HCl concentration was increased from 0 to 1 mol/L, the average degree of polymerization of cellulose decreased from 986 to 390. Although is known HCl to accelerate the acid degradation of cellulose, the increase in H⁺ concentration would cause H_2O_2 electro-synthesized by MGDE to decompose into O_2 and water, resulting in a decrease of the amount of hydroxyl radical. This is significant because hydroxyl radicals are another important factor in promoting cellulose degradation (Henriksson, Johansson, & Pettersson, 2000). Therefore, excess HCl is unnecessary for the degradation of the cellulose.

When the catalyst (EAQ) concentration of MGDE was increased, an increasing current response was observed as a consequence of a reduction of the overpotential for the formation of hydrogen peroxide, which meant that much more H₂O₂ was electro-produced. A decreasing DP of cellulose was simultaneously observed, which was convincing evidence that hydroxyl radical could accelerate the degradation of cellulose. There was a suitable potential for the production of H_2O_2 and FeCl₂ concentration for the conversion of H_2O_2 to hydroxyl radical (Fenton reaction). The excess of FeCl₂ might promote the decomposition of hydrogen peroxide into H_2O and O_2 and make the yield of hydroxyl radical decrease, this was disadvantageous for the degradation of cellulose. So the DP of the cellulose increased obviously when FeCl₂ concentration changed from 0.4 g to 0.5 g. The optimal conditions were established based on the results of the following experiments of Table 1: the potential vs. SEC was -1.2 V, the amount of FeCl₂ was 0.4 g, reaction time was 4 h, the corresponding DP of degraded cellulose was 156.

The suggested mechanism of cellulose degradation by hydroxyl radical is shown in Fig. 5. Initially, a hydrogen atom is extracted from C_4 of the glucose unit by the hydroxyl radical creating a carbon radical. This was oxidized with the formation of a superoxide anion, followed by a cleavage of the glycosidic bond (Henriksson



Fig. 6. Soluble sugar yield (A) and 5-HMF yield(B) after cellulose degradation.



Fig. 7. (A) The UV spectrum of 5-HMF. (B) The ¹H NMR spectrum of 5-HMF. (C) The ¹³C NMR spectrum of 5-HMF.

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The optimal experiments for degradation of cellulose with electro-Fenton method.^a

HCl (mol/L)	Electrode	Potential vs. SEC (V)	FeCl ₂ (g)	<i>T</i> (°C)	Time (h)	DP
1	5% MGDE ^b	-1.0	0	25	1	706
0	5% MGDE	-1.0	0.2	25	1	986
0.5	5% MGDE	-1.0	0.2	25	1	473
1	5% MGDE	-1.0	0.2	25	1	390
1.5	5% MGDE	-1.0	0.2	25	1	455
1	graphite	-1.0	0.2	25	1	663
1	0% MGDE	-1.0	0.2	25	1	598
1	1% MGDE	-1.0	0.2	25	1	507
1	3% MGDE	-1.0	0.2	25	1	473
1	7% MGDE	-1.0	0.2	25	1	540
1	10% MGDE	-1.0	0.2	25	1	516
1	5% MGDE	-1.0	0.2	25	2	350
1	5% MGDE	-1.0	0.2	25	4	230
1	5% MGDE	-1.0	0.2	25	5	238
1	5% MGDE	-1.0	0.4	25	4	185
1	5% MGDE	-0.5	0.4	25	4	243
1	5% MGDE	-1.5	0.4	25	4	297
1	5% MGDE	-1.2	0.4	25	4	156
1	5% MGDE	-1.2	0.5	25	4	209
1	5% MGDE	-1.2	0.4	25	5	157

^a 10 g cellulose was added into electrolyte for all experiments.

^b% MGDE means the content of EAQ in MGDE relative to conducting graphite.

et al., 2000). A C₁ carbon radical and an alkoxyl radical were formed on the new end groups, respectively. The former reacted with a hydroxyl radical to produce a hydroxyl group. The latter would react with a hydroxyl radical to produce an alkyl hydroperoxide (Graham Solomons & Fryhle, 2004). The alkyl hydroperoxide was transformed to a hydroxyl by reacting with two water molecules. Eventually, cellulose was partly converted to glucose and other sugars by electro-Fenton radical oxidation.

3.3. Production of soluble sugar and 5-HMF from cellulose

With the continuous reducing of DP, cellulose was converted to soluble sugar. The suspension was filtered through a filter membrane, then the filtrate was collected and the soluble sugar content in the supernatant was determined by the phenol–sulfuric acid method (Dubois, Gilles, Hamilton, Rebers, & Smith, 1956). The experimental results indicated that cellulose degradation with MGDE of 5% EAQ could produce more soluble sugar (molar yield 10.2%) than cellulose only treated in hydrochloric acid (molar yield 4.9%) when the reaction time for both was 4 h (see Fig. 6A).

The UV absorption spectrum for the filtrate was recorded, and distilled water was used as the blank. The supernatant liquid absorbed in the UV-vis range with maximum absorptivity at wavelength 284 nm (see Fig. 7A). This suggested that the product contained compounds with aldehyde functional groups. The supernatant liquid was then extracted with ethyl acetate several times. The combined organic layers were removed of solvent under reduced pressure distillation, and the residue was then purified via column chromatography on silica gel (eluent:petroleum ether/ethyl acetate = 20:1-5:1). This resulted in a yellow liquid, which was further characterized through ¹H NMR and ¹³C NMR. The results were as follows: ${}^{1}HNMR(CDCl_{3}, 400 MHz) \delta$: 4.054–4.087(t, 1H, CH₂OH),4.679 (s, 2H, CH₂OH), 6.510–6.519 (d, 1H, J=3.6 Hz, C=CH), 7.236-7.245 (d, 1H, /= 3.6 Hz, C=CH), 9.514 (s, 1H, COH); ¹³C NMR (CDCl₃, 400MHz) δ: 57.368, 77.169, 110.057, 152.186, 161.198, 177.906 (see Fig. 7B and C). Finally, the product was definitely as 5-hydroxymethylfurfural (5-HMF).

5-HMF has been traditionally obtained from monosaccharides. Cellulose is an especially promising source because it is a polysaccharide based on glucose units. However, the typical aqueous acid hydrolysis methods for producing 5-HMF from cellulose rely on high temperatures and pressures (250–400 °C, 10 MPa), resulting in yields of 30% (Scheirs, Camino, & Tumiatti, 2001). Fortunately, 5-HMF has been obtained from cellulose through our electro-Fenton methods. However, the largest molar yield of 5-HMF in electro-Fenton methods is only 5.6% (see Fig. 6.B), which is far from that of the typical aqueous acid hydrolysis methods, and there was 10.2% soluble sugar yield. The oxidation potential of hydroxyl radicals is so high that 5-HMF might be oxidized and decomposed into other substances when the reaction time is too long.

4. Conclusions

The graphite/PTFE electrodes modified by EAQ offer an alternative process for manufacturing H_2O_2 . The MGDE with 5% EAQ was applied in the degradation of cellulose with the electro-Fenton method. H_2O_2 generated by MGDE can react with Fe²⁺ to form hydroxyl radicals in an acidic medium, which can promote degradation of the cellulose. The optimal reaction conditions are established as follows: electrolysis potential -1.2 V, the reaction time 4 h and the FeCl₂ dosages 0.4 g. The DP of degraded cellulose was reduced to 156. The soluble sugar and 5-HMF were major products of the cellulose degradation and their total molar yield can reach up to 15.8%.

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