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Electrohydrogenation of 4-amino-5-nitrosodimethyluracil with a foamed nickel cathode

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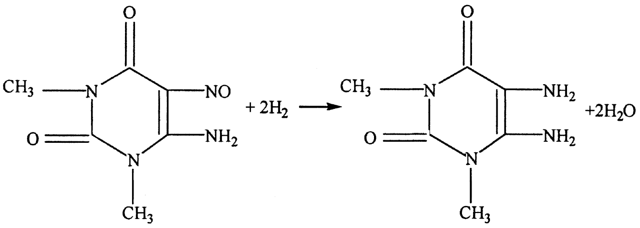
Abstract

The hydrogenation of 4-amino-5-nitrosodimethyluracil as an intermediate of commercially synthesized caffeine is generally carried out using iron powder reduction or Raney nickel catalyst. However, the iron powder results in serious pollution and the Raney nickel catalyst needs an expensive hydrogen supply system operated under severe conditions. A 'green' chemical technology using an electrohydrogenation process with a foamed nickel cathode was studied experimentally in a filter-press cell to eliminate the pollution and the unsafe conditions. The results showed that the electrohydrogenation process mainly depended on the pH of the catholyte, the current density and the temperature. All conversions for the pH range 2–8 were over 98%, but the current efficiency gradually decreased with increasing pH. For the current density range 84–420 A m^{-2} the conversion was over 98%, but the current efficiency decreased with increasing current density. The current efficiency improved with increasing temperature. The results show that to obtain a conversion of over 98% and a current efficiency of nearly 100%, the operating conditions should be pH 3–4, 84–168 A m^{-2} and 20–30 °C. The conversion and the current efficiency of the electrohydrogenation process were improved by using a foamed nickel cathode with a three-dimensional reticulated structure.

1. Introduction

Caffeine is widely used not only in pharmaceuticals but also in beverages as a nervous system stimulant and a diuretic. Caffeine is mainly produced by chemical synthesis, since the quality of caffeine extracted from tea is far below market requirements. The classic Traube's synthesis methods developed in 1900 has been used for commercial caffeine synthesis with the starting chemicals of urea, methylamine and chloroacetic acid with only a few improvements [1–3]. An important step in the synthesis process is that the intermediate 4-amino-5-nitrosodimethyluracil (ANDMU) is hydrogenated to form to the 4,5-diaminodimethyiuracil (DADMU) by the following reaction:



Iron powder was usually used as reductant in the hydrogenation, with electron transfer among the iron, hydrogen ions and ANDMU. The iron is oxidized to Fe_3O_4 in the reduction hydrogenation. Because of the low cost, iron powder is still used in some plants, although the hydrogenation efficiency is poor and a large amount of Fe_3O_4 in the form of a black slurry causes serious pollution. An alternative technique is catalytic hydrogenation using Raney nickel or a noble metal catalyst instead of the iron powder reduction process to improve the hydrogenation efficiency and control the pollution [4, 5]. The catalytic reaction is usually carried out in a stirred vessel at a pressure of 0.3 MPa and 60 °C in batch operation. But for the Raney nickel catalysis process, the hydrogen conversion is still low, with a large amount of hydrogen gas used to purge the batch operating system to produce a hydrogen atmosphere. An external hydrogen generation station is required to supply the hydrogen. The hydrogenation at high pressure also creates safety problems such as leakage, pumping, storage and explosiveness. Therefore, there is an urgent need for a 'green' chemical process with moderate operating conditions for controlling pollution and eliminating safety hazards.

ANDMU is slightly soluble in water so the hydrogenation process should operate in a slurry reactor. Catalytic hydrogenation is a heterogeneous catalysis reaction, which involves a series of steps, that is, hydrogen bubble dispersion in the suspended ANDMU solution, adsorption on the Raney nickel, hydrogen molecule dissociation and reaction of the atomic hydrogen with ANDMU. Another approach for ANDMU hydrogenation would be an electrohydrogenation process. Atomic hydrogen with high activity formed at the cathode of an electrolytic cell reacts directly with the ANDMU *in situ* without the gaseous hydrogen transport process. As pointed out by Yusem [6], in most cases the electrochemical hydrogenation products are similar to those obtained from high temperature and high pressure chemical catalytic reaction routes. No external hydrogen generation station would be needed for the electrohydrogenation, so the process will be environmentally ‘friendly’ and safe [7].

Analysis of the electrode processes for ANDMU electrohydrogenation studied by Dolgachev with polarography showed that three reduction waves at different pH values corresponded to three different species [8]. Gu’s work also demonstrated the same results [9]. ANDMU in aqueous solution exists in three forms, protonated, neutral molecules and anionic species, depending on the pH of the solution. The electrohydrogenation in an electrolytic cell was also studied by Dolgachev with several types of cathode such as platinum, nickel, graphite, copper, copper amalgam, tin, lead and mercury [10]. He showed that smooth nickel and nickel gauze were the best cathodes for hydrogenation. The nickel gauze had better conversion but lower current efficiencies. The hydrogenation process was improved with a high acidity solution of 5% H_2SO_4 or 2.5% HCl used in the catholyte, even though the current efficiency was only 80–87%. However, corrosion of the nickel cathode in H_2SO_4 or HCl was so serious that its application in practice was limited [10].

One of the newest types of porous, three-dimensional materials to receive attention is reticulated metal, which has interesting properties such as high specific surface area, isotropic electrical conductivity, high porosity, low electrolyte pressure drop and low effective density [11]. Foamed nickel is one type of reticulated metal with a porosity as high as 95–98%. Research on foamed nickel as an anode current collector or a substrate in nickel-metal hydride cells has been actively pursued in recent years [12–14], but few studies have been reported on the application of foamed nickel for hydrogenation. Although Raney nickel is a highly active catalyst for electrohydrogenation [6, 15–17], foamed nickel is better than Raney nickel in the view of its convenience, safety and low cost. The much higher specific surface area of foamed nickel relative to nickel gauze should reduce the current density at the cathode to reduce the polarization and improve the electroactivity and the current efficiency of the hydrogenation process.

The objective of this work is to study the feasibility of using a foamed nickel cathode for the ANDMU hydrogenation and to discuss the various factors affecting the electrohydrogenation process.

2. Experimental details

2.1. *Materials*

The foamed nickel used for the cathode was produced by the Beijing General Research Institute for Non-ferrous Metals. The specifications of the foamed nickel are listed in Table 1.

The foamed nickel of 2 mm thickness was processed with the desired corrugation which had different peak height and peak width as shown in Figure 1. The total size of each piece of corrugated formed nickel was 40 mm × 70 mm. The feeder electrode was a 160 mm × 70 mm nickel plate. Four pieces of the corrugated formed nickel were welded vertically to the feeder electrode. The sizes of the various corrugated foamed nickel cathodes are listed in Table 2.

The suspended ANDMU slurry flowed through the vertical flow channels between the corrugations to prevent plugging of the cathode. Preliminary tests used the double pieces of 3.5 mm thick foamed nickel as the cathode with two nickel wires welded between the two pieces to form a vertical channel. The anode was a lead plate.

The ANDMU was an intermediate product of a caffeine synthesis plant and was purified by washing

Table 1. Foamed nickle specifications

Nickel content	>99%
Pore size	200–500 μm
Porosity	>95%
Resistivity	<9 × 10^{-6} Ω m

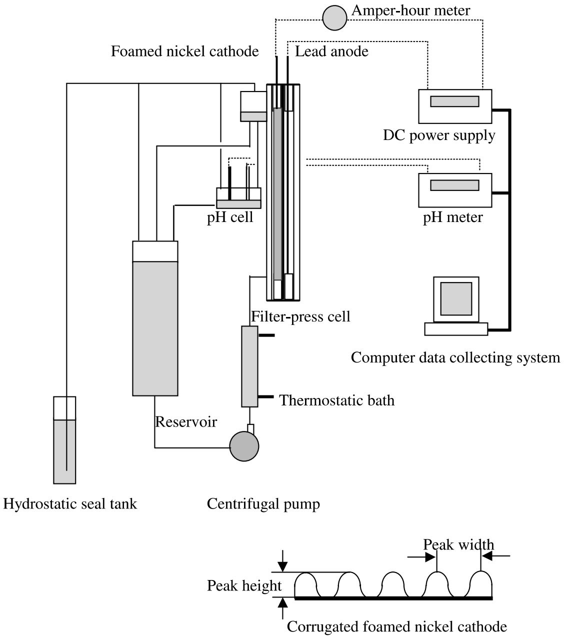


Fig. 1. Experimental apparatus for electrohydrogenation.

Table 2. Size parameters for the corrugated foamed nickel cathode

	Thickness /mm	Peak height/mm	Peak width/mm
Foamed nickel cathode 1	2	10	10
Foamed nickel cathode 2	2	10	5
Foamed nickel cathode 3	3.5*	–	–

* Double pieces.

with deionized water. The ANDMU content was 0.95–0.98 as determined by thermogravimetry and HPLC. All other chemicals were reagent grade produced by the Beijing Chemicals Corporation.

2.2. *Apparatus*

A filter-press cell was made of plexiglass with a cathode chamber 50 mm × 100 mm × 20 mm and an anode chamber size 50 mm × 100 mm × 25 mm. A cation-exchange membrane (Fushun Chem. Co., China) was inserted between the two chambers. The cathode chamber outlet had an overflow weir to keep the catholyte head constant. The reservoir volume was about 800 ml. The catholyte loop consisted of a cathode chamber, a storage tank, a thermostatic bath, a pH detector cell and a magnetic pump which recirculated and slurried the ANDMU suspension solution. The catholyte loop was sealed by a hydrostatic cell which kept the loop under a hydrogen atmosphere. To simplify the process, the anolyte was not circulated in the experiments. The catholyte cell had a vent to atmosphere with a hydrostatic seal tank to eliminate the build-up of hydrogen gas. A schematic of the system is shown in Figure 1.

The electrolyte cell was supplied by a 10 V d.c. power supply which provided either constant current or constant voltage. An electronic ampère-hour meter was used to determine the charge passing through the cell to calculate the current efficiency for each run. The catholyte pH and the cell voltage were recorded by a computerized data collecting system.

2.3. *Experimental procedures*

Each run was operated in batch recirculation at constant current. The ANDMU was dried, weighed and ground to fine powder. Before adding ANDMU to the reservoir, the catholyte was electrolysed for about 30 min to fill the catholyte system with hydrogen. The catholyte flow rate was so high that the fine ANDMU particles were kept in suspension. During the electrolysis, the catholyte pH increased due to the consumption of hydrogen ions, so the catholyte pH was adjusted to the required value by adding H_2SO_4 to the reservoir. The ANDMU concentration in the slurry catholyte was 1–20 g l^{-1}. The ANDMU and DADMU concentrations were measured during the experiment by taking samples from the reservoir. The run was terminated when the ANDMU and DADMU concentration was constant.

2.4. *Analysis methods*

A Shimadzu Liquid Chromatograph with a Shimpack VP-ODS 4.6 mm × 150 mm column was used to determine the ANDMU concentration of the hydrogenation solution. The mobile phase was 30 vol % acetonitrile and 70 vol % water, operated at 25 °C and 77 bar with a flow rate of 0.7 ml min^{-1}, and measured by a u.v. detector at 254 nm. The hydrogenation product DADMU was analysed by diazotization titration. The titration end point was determined by the dead-stop method and checked with KI-starch indicator. A 752C u.v. spectrophotometer was used to determine the ANDMU and DADMU absorption spectra. The conversion was calculated based on the moles of the DADMU product formed in the electrohydrogenation divided by the moles of the original ANDMU.

3. Results and discussion

3.1. *Voltammograms of electrolytic cell*

In preliminary tests, voltammograms of the electrolytic cell were recorded using the three foamed nickel cathodes listed in Table 2 and a plain nickel electrode in the absence of ANDMU. The supporting electrolyte for the catholyte was 1 wt % $(NH_4)_2SO_4$ solution while that for the anolyte was 5 wt % $(NH_4)_2SO_4$ solution. The aim of the preliminary tests was to compare the voltametric behaviour of the three foamed nickel cathodes for water electrolysis (hydrogen evolution at the cathode and oxygen evolution at the anode).

The results shown in Figure 2 show that the cell currents of all three foamed nickel electrodes having larger specific surface area were higher than for the plain nickel electrode at the same cell voltage. The foamed nickel cathode 2, having the largest specific surface, had the largest cell current at the same cell voltage, since the current density and the polarization decreased due to the larger specific surface area of the foamed nickel cathode. When the $(NH_4)_2SO_4$ concentration was increased to 3 wt % in the catholyte, the cell current and cell conductivity did not increase remarkably. For the electrolysis of water, the cell current did not change significantly with increase in catholyte flow rate. The results show that the process was not dominated by transport process or gaseous hydrogen evolution at the cathode. The foamed nickel cathode 2, having the largest surface area, was selected for the remaining experiments.

3.2. *Chemical behaviour of DADMU*

The ANDMU and DADMU u.v. absorption spectra in aqueous solution were measured at pH 7 and had maximum absorption peaks at 224 and 272 nm, respectively. The u.v. absorption peak red-shifted during the

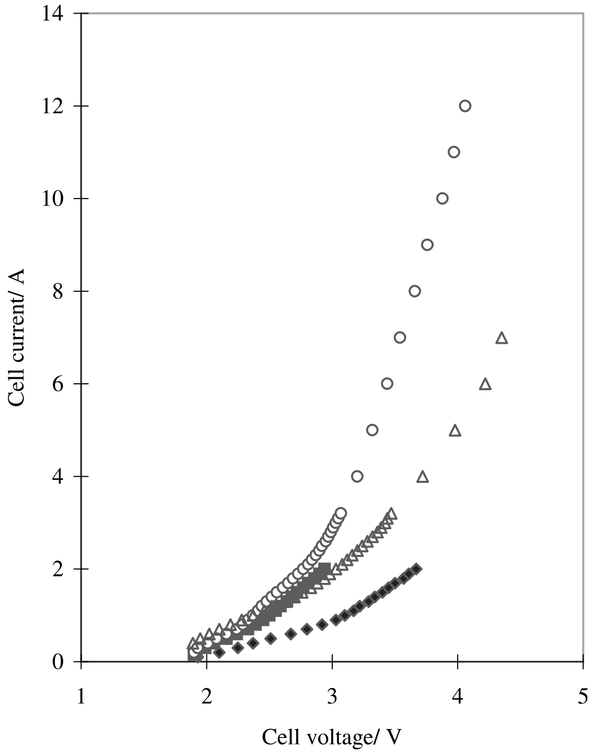


Fig. 2. Voltammograms of the foamed nickel cathode in the filter-press cell. Key: (◆) plain Ni cathode; (■, ○, △) foamed Ni cathodes 1, 2, 3, respectively.

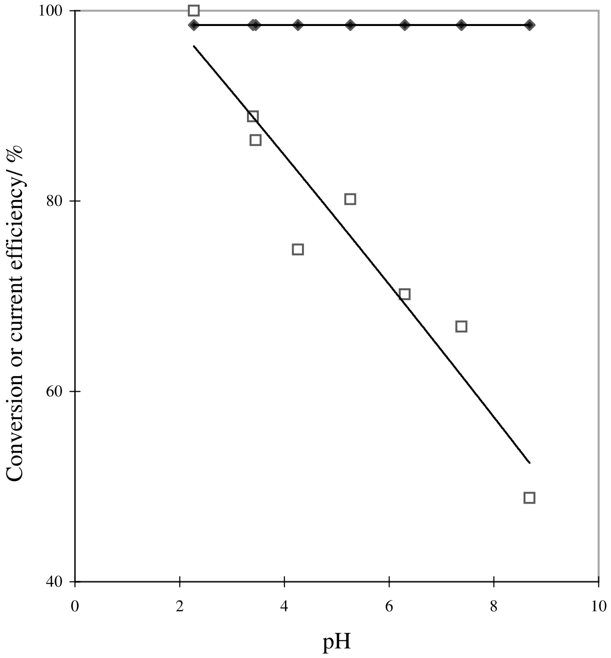


Fig. 3. Effect of catholyte pH on conversion (◆) and current efficiency (□) for ANDMU concentration of 2 g l^{-1} at 20 °C.

hydrogenation process. The hydrogenation product, DADMU, was found to be unstable in air, as shown by the colour change of the solution exposed to air at the end of each run which changed gradually from colourless to violet at lower pH (about 4). The instability was also confirmed by the decay of the hydrogenation product peak, DADMU, in the HPLC analysis. Another group of tests was carried out for further analysis. The solution was covered with a cyclohexane layer about 1 cm in thickness to reduce the effect of air on the aqueous DADMU solution. The results showed that the DADMU in the solution was basically stable for about three hours at pH 8 and 20 °C but the DADMU would slowly decay even without contact with air. The DADMU solution stability was affected by the acidity in a similar way to 5,6-diaminouracil [18, 19], which becomes oxidized and hydrolysed in a different pH range. The decomposition may be due to the effect of the 1,3-dimethyl on the uracil. To obtain higher hydrogenation conversion, the stability of the DADMU in solution should be considered and the electrolytic hydrogenation cell should work in a hydrogen atmosphere to slow the degradation.

3.3. *pH effect*

The ANDMU electrohydrogenation conversion and the current efficiency were measured in the pH range 2–8. The nickel cathode at $pH < 2$ was badly corroded and the ANDMU is unstable at $pH > 8$ [8, 9]. All runs used an ANDMU concentration of 2 g $l^{-1}$and a cathode current density of 84 A m^{-2} at 20 °C. The results shown in Figure 3 show that the conversions for the pH range 2–8 were all over 98%, but the current efficiency gradually decreased with increasing pH; thus to obtain the same conversion at a given current density, the electrolysis time must be prolonged. The results may be explained as follows. The form of ANDMU existing in the aqueous solution mainly depends on the pH [8]. Lower pH favours the protonation of ANDMU which, in comparison with the neutral and anionic species, has a positive charge which facilitates electron transfer at the foamed nickel cathode to accelerate the electrohydrogenation process. Therefore, the electrohydrogenation time for conversion of over 98% was longer at higher pH. The current efficiency mainly depended on the competition between the electron transfer of the protonated ANDMU and hydrogen ion discharge at the cathode. If the hydrogenation reaction rate is lower than the hydrogen production rate at the cathode, the excess hydrogen will evolve as bubbles. Furthermore, for long reaction times the decay of the hydrogenation product DADMU will be significant. The DADMU decay product can be hydrogenated again to form DADMU, but it will consume more electrons and reduce the current efficiency. Although lower pH will favour the conversion and the current efficiency, the pH in practice will be limited by the corrosion of the nickel cathode. Therefore, a pH range 3–4 is suggested for the electrohydrogenation process to obtain a good conversion and adequate current efficiency.

3.4. *Current density effect*

The conversion and the current efficiency for the ANDMU electrohydrogenation process in the electrolytic cell were measured at different current densities by changing the cell voltage. All runs were conducted in suspension with ANDMU in suspension at a concentration of 6 g l^{-1} at pH 3 and 20 °C. The current density was the apparent density based on the cathode size. The results showed that for the range 84–420 A m^{-2}, the conversion was unchanged while the current efficiency decreased with increasing current density as shown in Figure 4. The current efficiencies for the electrohydrogenation for over 98% conversion of 6 g l^{-1} ANDMU were 100% for current densities lower than 168 A m^{-2}. The unchanged, high conversion showed that almost no ANDMU hydrogenation by-product was produced in the operating range. This was confirmed by the absence of by-product peaks in the HPLC analysis. When the current density was higher than 168 A m^{-2}, the current efficiency gradually dropped to about 50%. In practice, the current density should not be higher than 168 A m^{-2} for good conversion and current efficiencies. The low current density will increase the cell cost, but it will reduce pollution and give good conversion and current efficiency, so the low current density may be acceptable for commercial application.

3.5. *Temperature effect*

To observe the effect of temperature, a group of tests was carried out for temperatures from 20–50 °C. The other parameters for each run were fixed with an ANDMU concentration of 2 g l^{-1}, pH 8, a current density of 84 A m^{-2} and a supporting electrolyte $(NH_4)_2SO_4$ concentration of 10 g l^{-1}. The ANDMU conversion and the current efficiency in Figure 5 show that over 98% conversion of ANDMU could be obtained for the temperature range 20–50 °C at pH 8, with the current efficiency improved at higher temperatures. The reactions at the cathode mainly include ANDMU hydrogenation and hydrogen evolution, which reduces the current efficiency. The increased temperature accelerated the ANDMU hydrogenation reaction more than the hydrogen evolution, although both were accelerated at elevated temperatures. The improved current efficiency is again the result of competition between the two reactions.

The experiments also showed that cell voltage decreased with increasing temperature, because the conductivity of the supporting electrolyte increased with temperature. The cell operation should be at a slightly higher temperature to decrease the cell voltage, but the cell temperature is limited, not only by the degradation of the hydrogenation product DADMU, but also by the stability of the anode and the polymer membrane. As a result, 40 °C is proposed for the electrohydrogenation process.

3.6. *Electrohydrogenation time for different ANDMU concentrations*

The solubility of ANDMU in water was determined as shown in Figure 6. In the pH range 3–8 the ANDMU solubility does not change significantly. The catholyte was an aqueous slurry of suspended ANDMU particles, and since the electrohydrogenation product DADMU is soluble, the slurry particles gradually dissolve during the

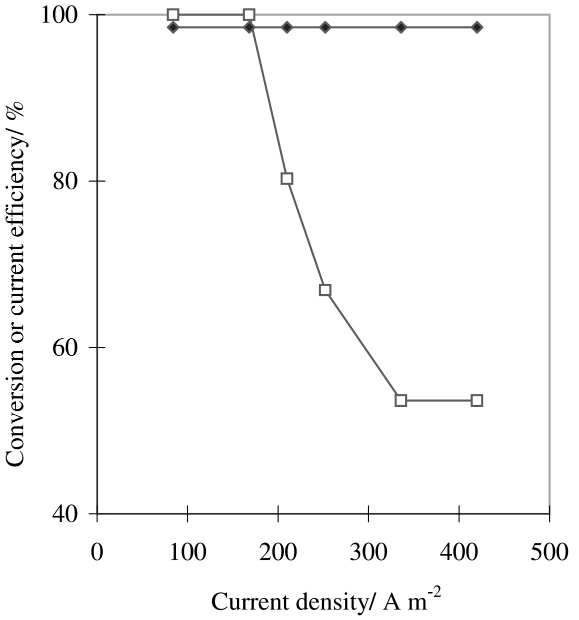


Fig. 4. Effect of current density on conversion (◆) and current efficiency (□) for ANDMU concentration of 6 g l^{-1} at pH 3 and 20 °C.

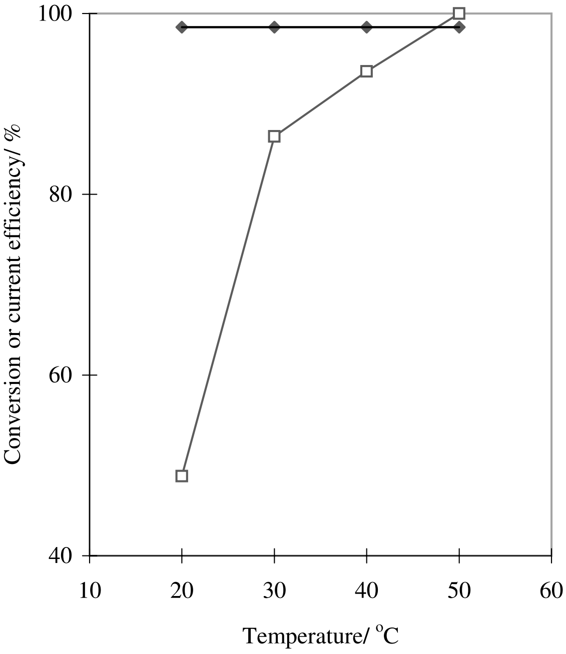


Fig. 5. Effect of temperature on conversion (◆) and current efficiency (□) for ANDMU concentration of 2 g l^{-1} and current density of 84 A m^{-2} at pH 8.

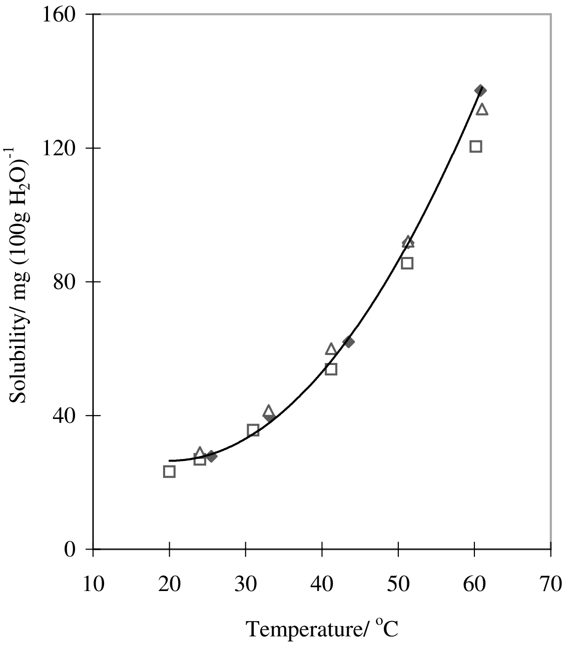


Fig. 6. Solubility of ANDMU at pH 3.0 (◆), 5.7 (☐) and 8.0 (△).

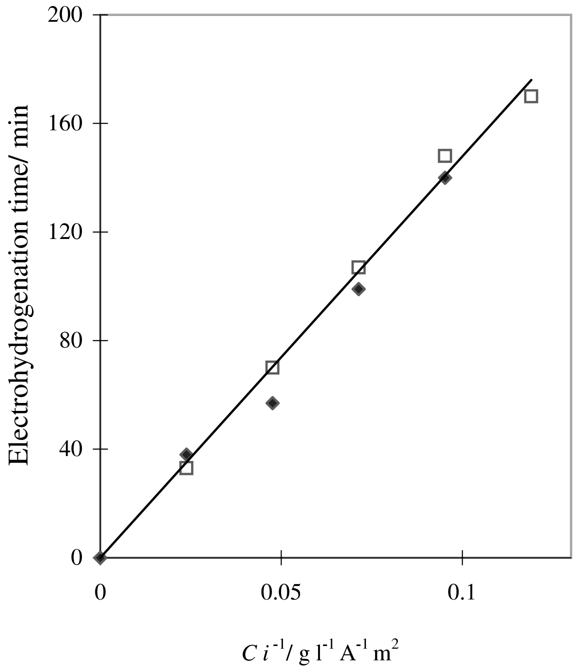


Fig. 7. Electrohydrogenation time against ANDMU concentration and current density. Key: (◆) 84 A m^{-2} and (☐) 168 A m^{-2}.

process. The effect of the suspended ANDMU concentration on the electrohydrogenation time for the conversions over 98% and current efficiencies of nearly 100% was determined for current densities of 84 and 168 A m^{-2} and pH 3. The results showed that the electrohydrogenation time was proportional to the suspended ANDMU concentration, C, divided by the current density, i, as shown in Figure 7. The time τ (min) was given by

$$\tau = \frac{vrnF}{60eAM} \times \frac{C}{i} \tag{1}$$

where v is the catholyte volume, r is the conversion, n is the transfer electron number, F is the Faraday constant, e is the current efficiency, A is the cathode area and M is the ANDMU molecular weight. The measured times were very close to the values predicted by Equation 1, which shows that the electrohydrogenation rate is dependent on the current density. In general, the heterogeneous electrohydrogenation reaction included the following steps: dissolution of the suspended ANDMU particles, mass transfer of reactant ANDMU and product DADMU in solution and electron transfer on the cathode surface. Based on polarographic data at a mercury cathode, Avrutskaya suggested that the ANDMU electrohydrogenation is a four-electron transfer process accompanied by a dehydration reaction [20]. The experimental results suggest that the electron transfer may be the controlling step for these conditions.

3.7. *Cell voltage*

The cell voltage in the constant current electrolysis was measured during batch electrohydrogenation. In a group of tests the catholyte pH was changed from 2.2 to 8.2, with all other parameters kept constant, such as the current density of 84 A m^{-2}, the ANDMU concentration of 2 g l^{-1}, the $(NH_4)_2SO_4$ concentration of 10 g l^{-1} as the supporting electrolyte and the temperature of 25 °C. The constant cell current of 1 A was maintained for each run. Typical cell voltage-time graphs are given in Figure 8. The initial cell voltage on the curve corresponded to the cell voltage for hydrogen electrolysis at the cathode before the addition of ANDMU. When ANDMU was added to the catholyte, the cell voltage dropped suddenly, then remained constant for some time. The cell voltage then increased gradually to the initial cell voltage when the hydrogenation process was finished. For the constant current electrolysis the cell voltage decrease, Δv, was related to the pH of the catholyte as shown in Figure 9. The cell voltage decrease is mainly due to the ANDMU hydrogenation potential and the polarization potential, because the ANDMU is a nonelectrolyte and does not contribute to a decrease in cell ohmic resistance. Unfortunately, at present no standard data is available for the ANDMU hydrogenation potential and the polarization potential. The hydrogenation potential and the kinetics behaviour of the electrohydrogenation process will be studied in future work.

4. Conclusions

ANDMU electrohydrogenation, which is an intermediate step in the commercial synthesis of caffeine, has been studied experimentally in a filter-press cell with a

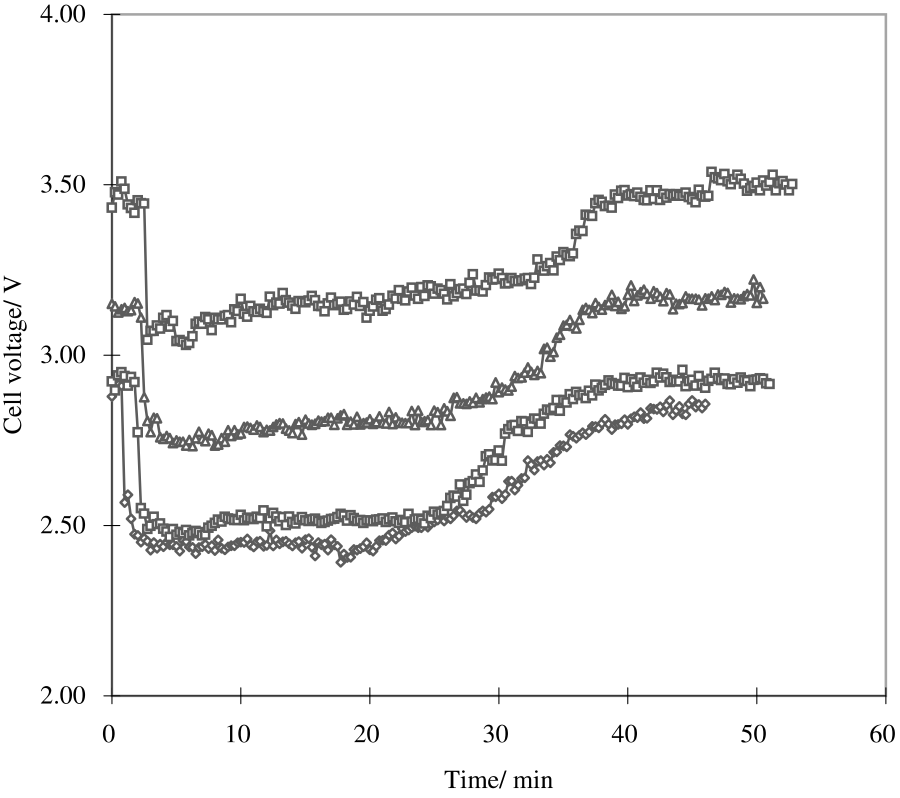


Fig. 8. Typical cell voltage against time curve at constant cell current of 1 A, ANDMU concentration of 2 g l^{-1}, pH 4 (○), 5 (□), 6 (△), 7 (□) and 25 °C.

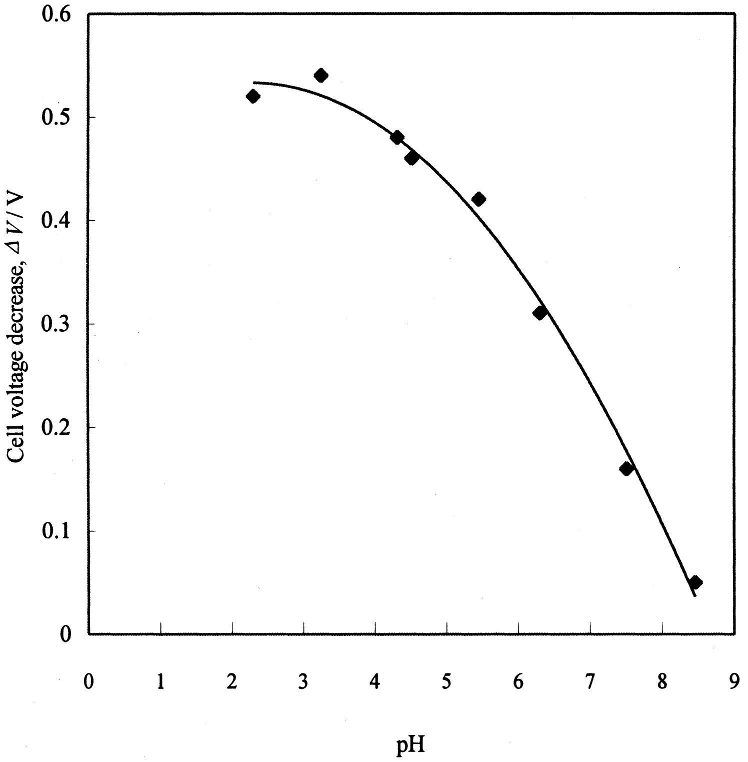


Fig. 9. Cell voltage decrease, ΔV against pH of catholyte for ANDMU concentration of 2 g l^{-1}, current density of 84 mA^{-2} and 25 °C.

foamed nickel cathode having a reticulated three-dimensional structure. The results show that ANDMU can be hydrogenated at the foamed nickel cathode with high conversion and high current efficiency. The main factors influencing the conversion and current efficiency are catholyte pH, current density at the cathode and temperature. Conversions of over 98% and current efficiencies of 95–100% were obtained with the following conditions: pH 3–4, $i = 84$–$168\ \mathrm{A\ m^{-2}}$ and $T = 20$–30 °C. The current efficiency decreased with increasing pH and current density, but the current efficiency increased with increasing temperature to 40 °C. Considering the stability of the polymer membrane and the lead anode, the proposed operating temperature should not be over 40 °C.

The electrohydrogenation with the foamed nickel cathode will produce much less pollution than the chemical reduction of ANDMU with iron powder, ANDMU can also be hydrogenerated with the inexpensive foamed nickel cathode under more moderate conditions than chemical catalysis using Raney nickel without the need for an auxiliary hydrogen supply station. So this process is a 'green' chemical technology having good potential applications. In the experiments the foamed nickel cathode was not poisoned and significantly corroded. Further scale-up research is needed for commercial application.

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