CHAPTER II

Model Studies of Application of Electrocoagulation

1. Electrocoagulation unit

An electrocoagulation reactor was made from an electrolytic cell with one anode and one cathode. A pair of conductive metal plates was connected to a power supply as shown in Figure 1. The conductive metal plates are commonly known as 'sacrificial electrodes', which are made up of the same materials such as aluminium, iron, copper, zinc, platinum and titanium.[1-2] Each electrode serves a specific application. However, a universal electrode, Al or Fe, is generally used due to its availability and low cost. The electrodes were dipped into the solutions.

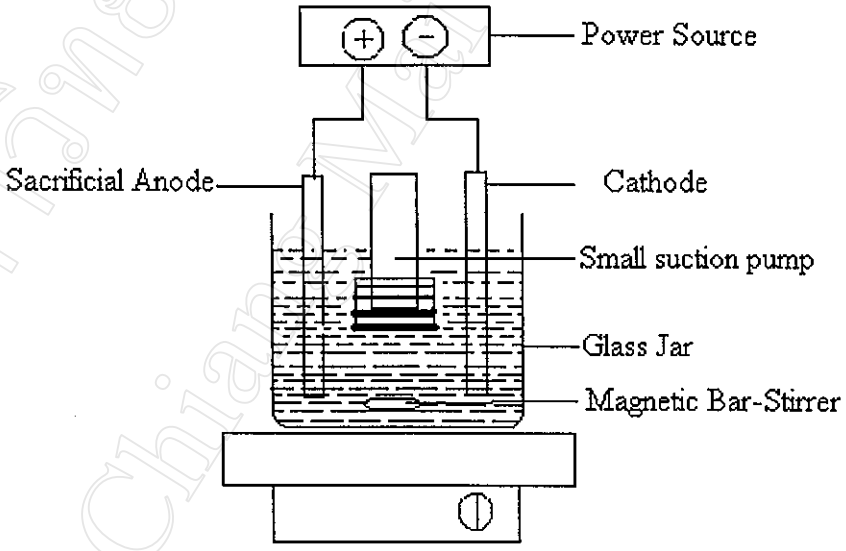


Figure 1. Bench-scale Electrocoagulation reactor with electrode and a small suction pump (For solution sampling).

An electric current was applied to the electrodes to start the electrocoagulation. In almost every case, a direct current (DC) was used.[1-3] However, an alternating current (AC) has sometimes been used in some industrial process.[2,4] During the electrocoagulation process, supporting electrolytes such as Na_2SO_4,[5]

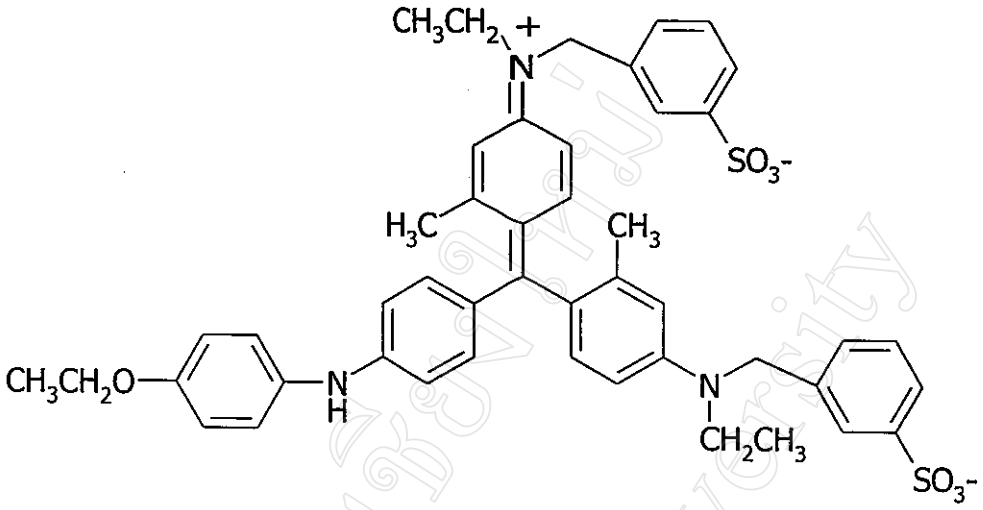
NaCl,[1-4] HCl [6] or H_2SO_4 [7] were added into the solutions. In this model studies chapter, the electrocoagulation unit was set up as in Figure 1. A direct current was applied through the electrodes. Al or Fe was used as the sacrificial electrodes and NaCl was used as a supporting electrolyte since it is cheap and non-toxic.

The main aim of the work presented in this chapter was to investigate the potential of the electrocoagulation process to remove certain unwanted substances using model studies.

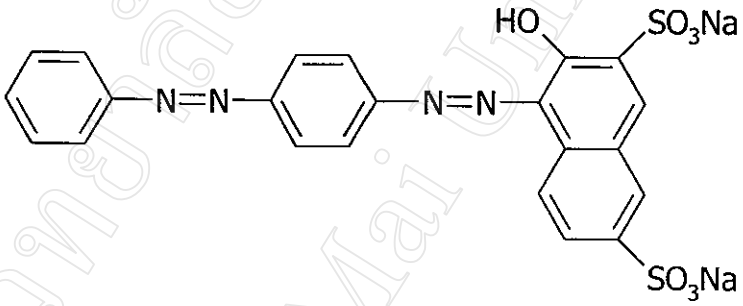
2. Model studies

2.1 Preliminary Investigation of Electrolytic Decolourization

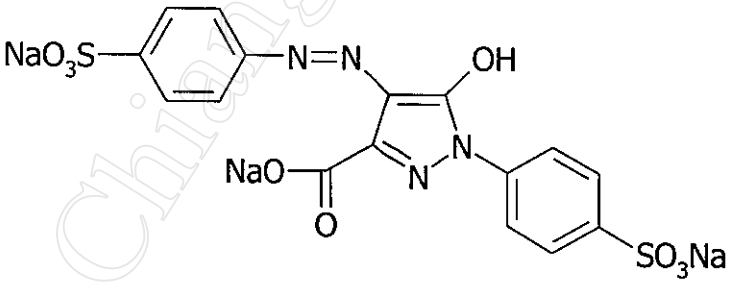
The first model studies of the electrocoagulation have been carried out using synthetic and natural dyes. The objective of this model studies was to investigate the electrolysis behaviour of dye solutions. The synthetic dyes, brilliat blue FCF, ponceau 4R and tartrazine 10140 were dissolved in aqueous solutions. However, curcumin, a natural dye, dissolved only slightly in aqueous solution. Therefore, Tween 40, a surfactant (1% v/v), was added to help curcumin dissolve in the aqueous solution. The dye solutions were placed into the electrocoagulation unit using aluminium plates as electrodes. Sodium chloride (NaCl, 2g/L) was added as an electrolyte and a direct current (0.5 A, 22 V) was applied. The scale of these studies was 1 liter and the solutions investigated in these studies were prepared using pure chemicals.



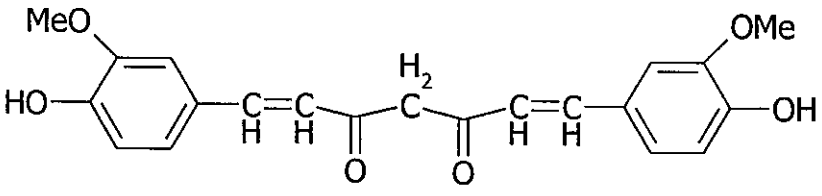
Brilliat Blue FCF



Ponceau 4R



Tartrazine 10140



Curcumin

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The absorbance values of dye solutions after electrolysis were shown in Table 1.

Table 1. The absorption of dye solutions after electrocoagulation*.

Dye solutions	λ_{max} (H_2O)	Abs	
		before electrolysis	after electrolysis
1. Brilliat Blue FCF	628	2.80	0.024
2. Ponceau 4R	504	2.15	0.008
3. Tartrazine 10140	428	2.40	0.028
4. Curcumin	430	2.67	2.22

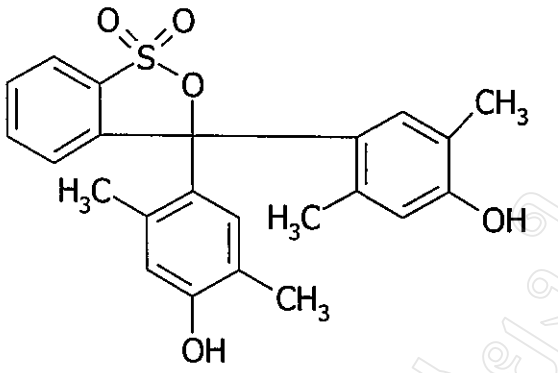
*the results obtained after a double electrolysis for 1.5 and 0.5 hours

The absorbances of the solutions were measured 2 hours after applying the current. It can be seen clearly that after electrolysis, a large proportion of colour had been removed, since the absorbances of these solutions dropped dramatically, as shown in Table 1. With the exception of curcumin, the preliminary results revealed that the electrocoagulation method had a good decolourization efficiency. Therefore, this method was worthy of further study.

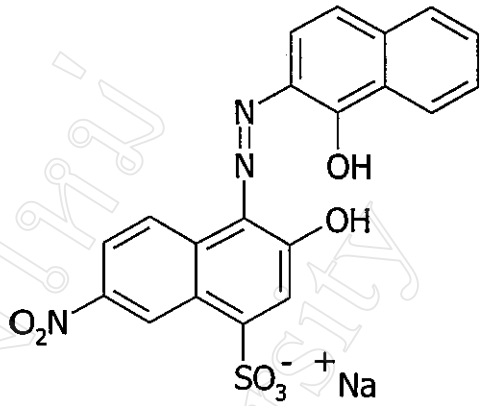
2.2 Electrocoagulation of dyes

2.2.1 Synthetic dyes

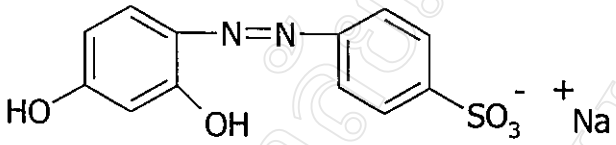
The solutions of synthetic dyes, xylenol blue, eriochrome black T, tropaeoline O and a phenolic compound, *O*-nitrophenol were studied for the decolourization.



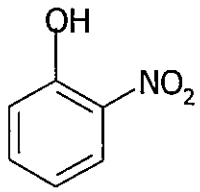
Xylenol blue



Erichrome black T



Tropaeolin O



O-nitrophenol

To a solution of dyes (0.01% w/v) in water (1 L) was added NaCl (2g) as an electrolyte. A direct current (0.5 A, 22 V) from a DC power supplier was then passed through the solution *via* two aluminium electrodes. At 15 minutes intervals during the 2 hours period of the electrolysis, a 10 cm^3 aliquot sample of the solution was taken, and filtered. The absorbances were measured at an appropriate wavelength of the absorbance maximum (λ_{max}) for each compound, as follows : 424, 503 and 486 nm for xylenol blue, eriochromeblack T and tropaeoline O, respectively. However, the wavelength (λ_{max}) for *O*-nitrophenol fluctuated, probably due to the nature of the compound during electrolysis. Therefore, the λ_{max} of *O*-nitrophenol was measured in the range of 266-285 nm. The plots between the absorbances *versus* the eletrolysis times for each compound are shown below (Figures 2-5).

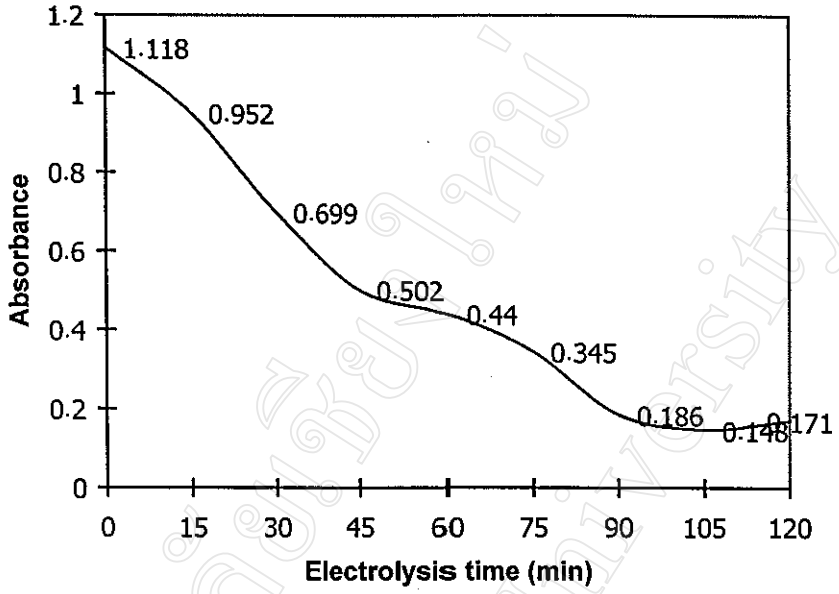


Figure 2. Plots of absorbance and electrolysis time, 0.01% w/v of xylenol Blue, 424 nm

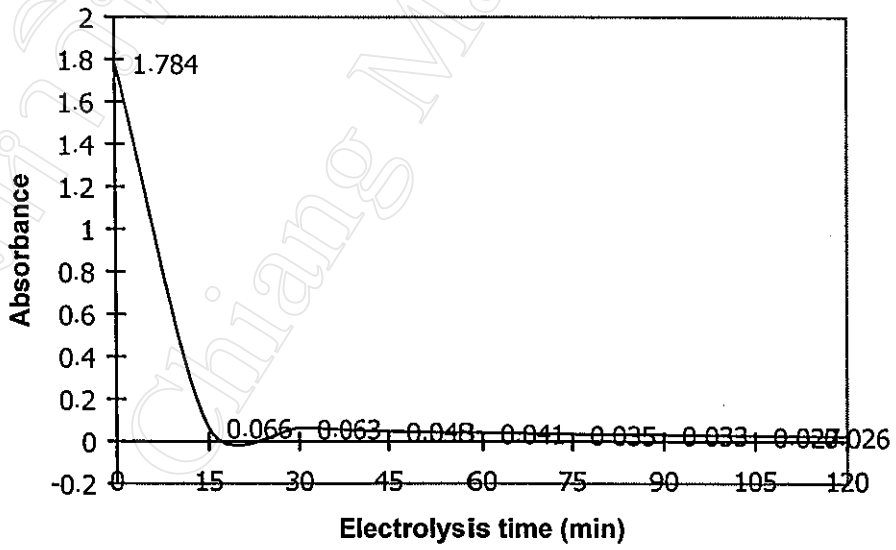


Figure 3. Plots of absorbance and electrolysis time, 0.01% w/v of eriochromeblack T, 503 nm

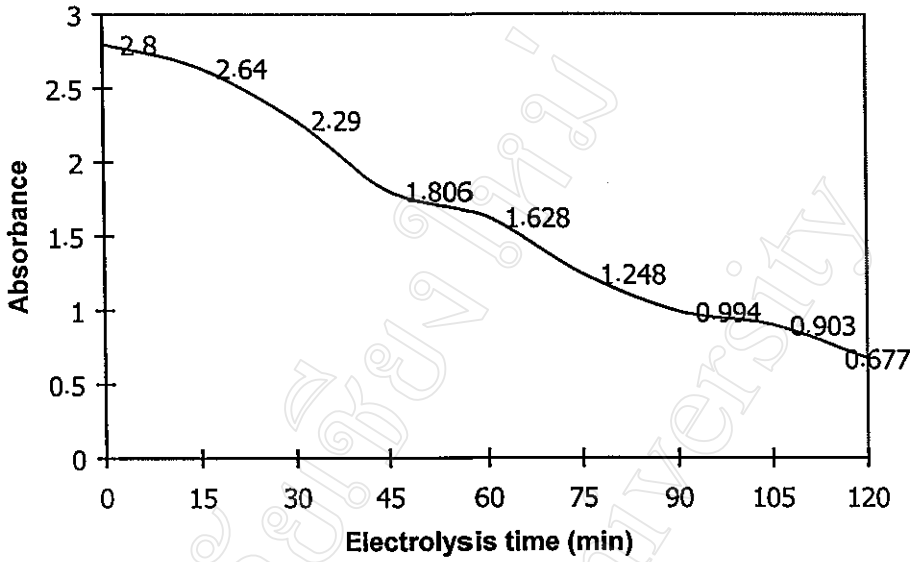


Figure 4. Plots of absorbance and electrolysis time, 0.01% w/v of tropaeoline O, 486 nm

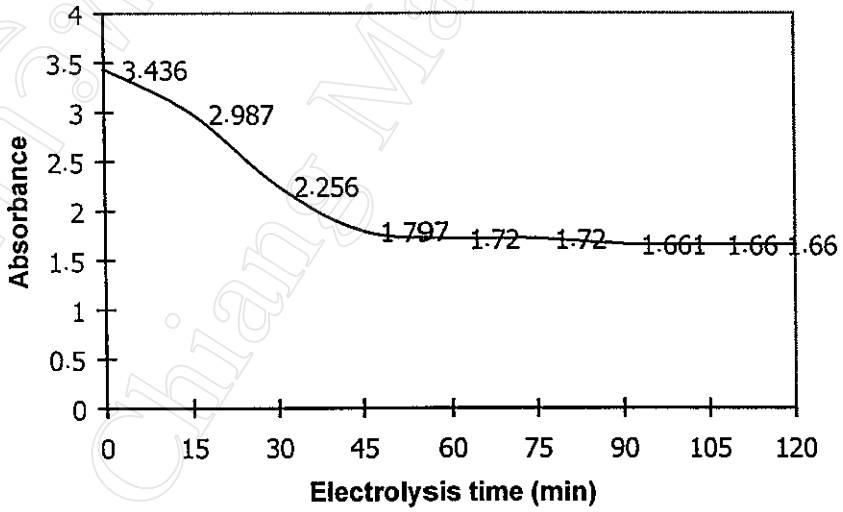


Figure 5. Plots of absorbance and electrolysis time, 0.01% w/v of *O*-nitrophenol, 266-284 nm

In case of *O*-nitrophenol, the absorbance detected in each electrolysis time was measured at the λ_{max} shown below.

Time	0	15	30	45	60	75	90	105	120
λ_{max}	266	281	283	282	283	285	285	284	284

From Figures 2-5, the measured absorbance for each electrolysis time was converted to the residual weight percentage of the compound by a calibration curve obtained from a plot between the absorbance *versus* the concentration of each dye. A plot of concentration and electrolysis time for each dye was then obtained as shown in Figure 6.

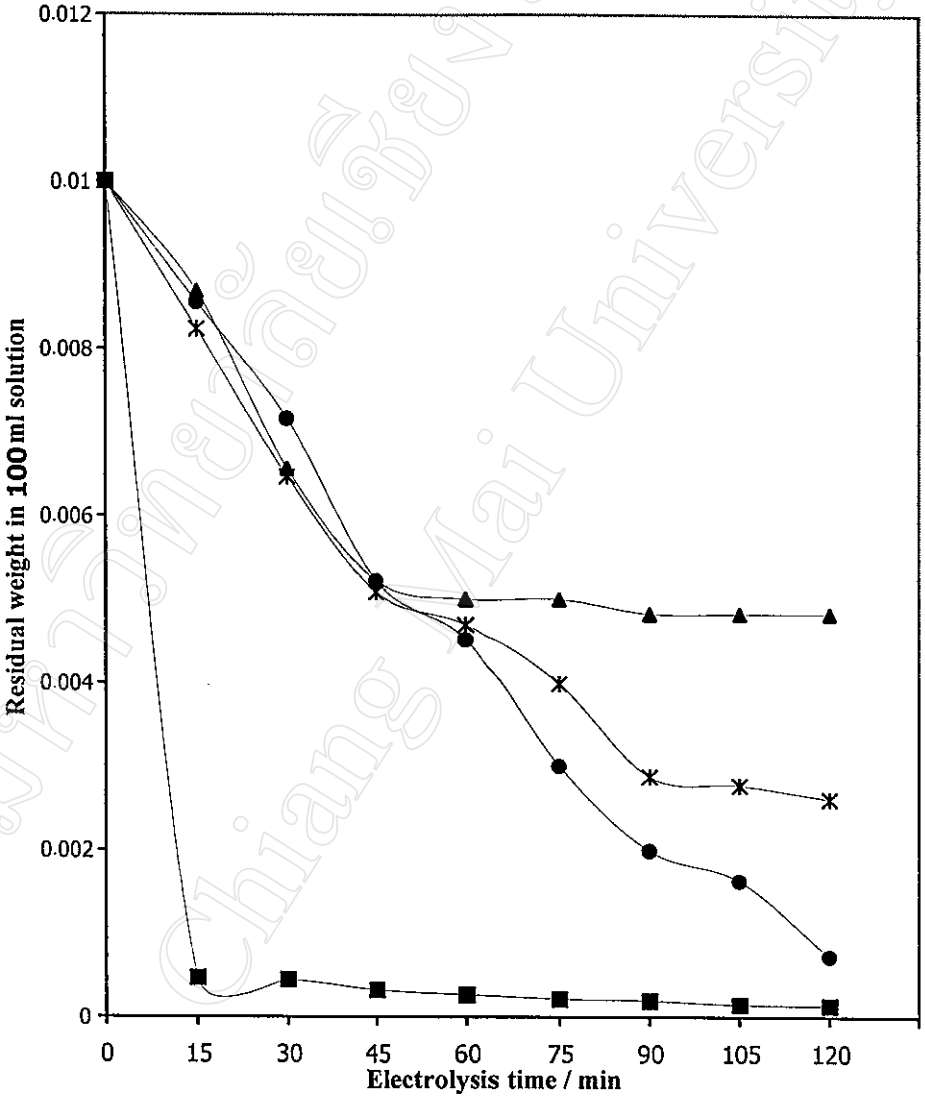


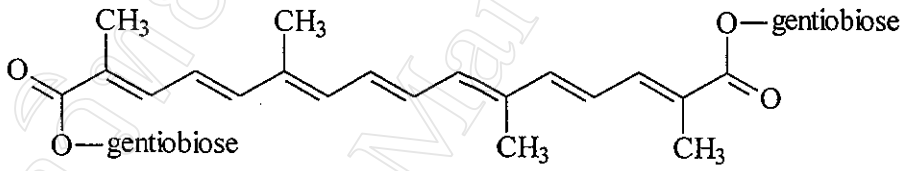
Figure 6. Plot of the residual weight percentage and electrolysis time for ∗, xylenol blue; ■,eriochrome black T; ●,tropaeolin O and ▲,*O*-nitrophenol.

It can be seen that after the electrocoagulation, the concentrations of xylenol blue, eriochromeblack T, tropaeoline O and *O*-nitrophenol were lower than the

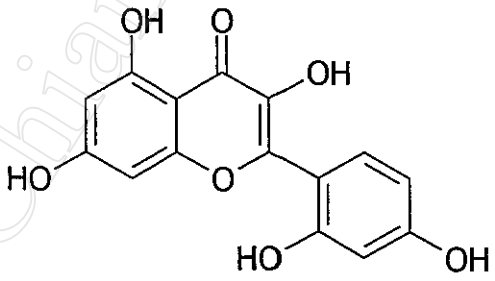
concentration before electrocoagulation. The percentage removal were : xylenol blue (84.7%), eriochrome black T (98.5%), tropaeoline O (75.8%) and *O*-nitrophenol (51.7%). The decolourization efficiency was due to the formation of $Al(OH)_3$ is a gelatinous precipitate which adsorbs dyes and precipitates out of solution. From structural considerations, the Al^{3+} can also complex with ions of opposite charge and precipitate out of solution. On the other hand, the phenol part can also form insoluble complexes with Al^{3+} that precipitate out of the solution.

2.2.2 Natural dyes

The solutions of natural dyes namely crocin, morine and curcumin were treated by the electrocoagulation method.



crocin



morin

The separation of the dyes by electrochemically-generated coagulant was carried out in a glass jar with aluminium electrodes. An aqueous solution (1 L) containing a dye (0.01% w/v of crocin or morin, or 0.1 and 0.2% w/v of curcumin in 5 % potassium oleate) and NaCl (2 g) as an electrolyte were mixed in the jar. Direct current (0.5 A, 22 V) from a DC power supplier was then passed through the solution

via two aluminium electrodes. At 15 minute intervals during the 2 hours period of electrolysis, a 10 cm^3 aliquot sample of the solution was taken, and filtered. The absorbances were measured at an appropriate wavelength of the absorbance maximum (λ_{max}) for each compound, as follows: 464, 262 and 454 nm for crocin, morin and curcumin, respectively. The plots between the absorbances *versus* electrolysis time for each compound are shown below.

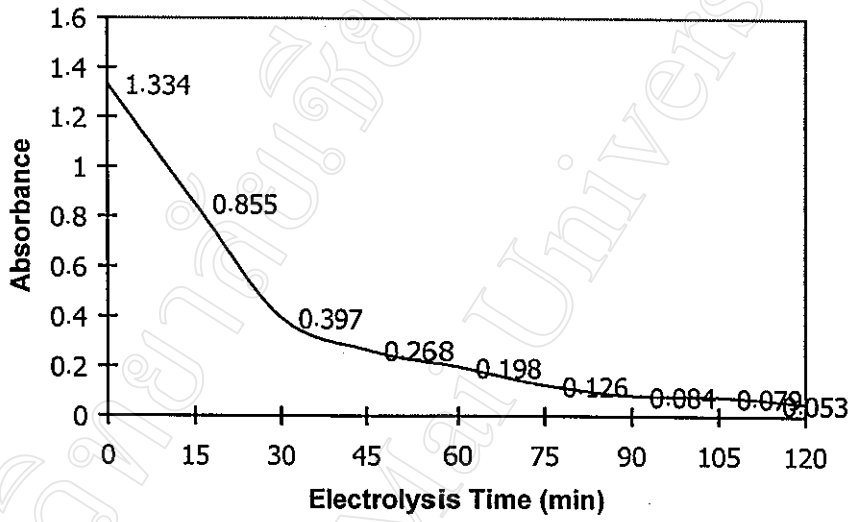


Figure 7. Plots of absorbance and electrolysis time, 0.01% w/v of crocin, 464 nm

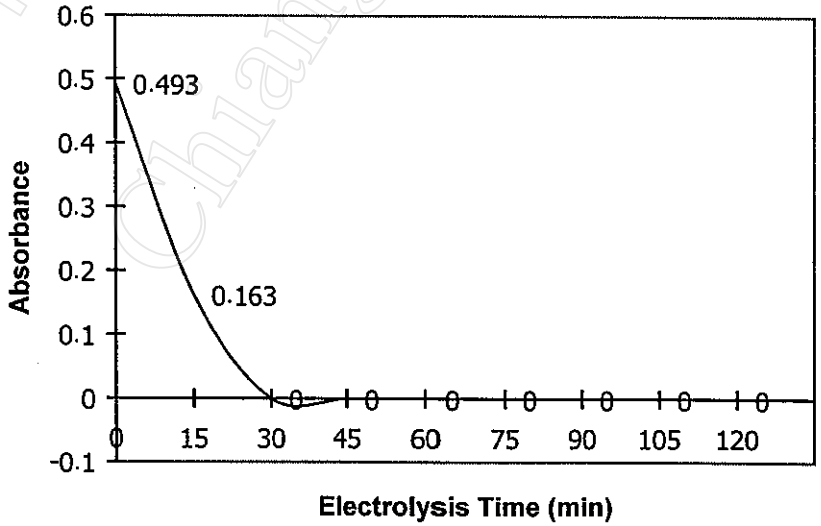
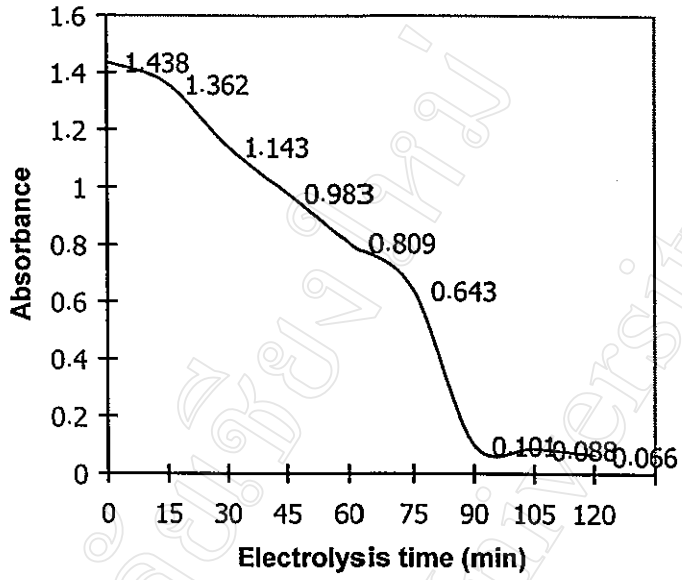
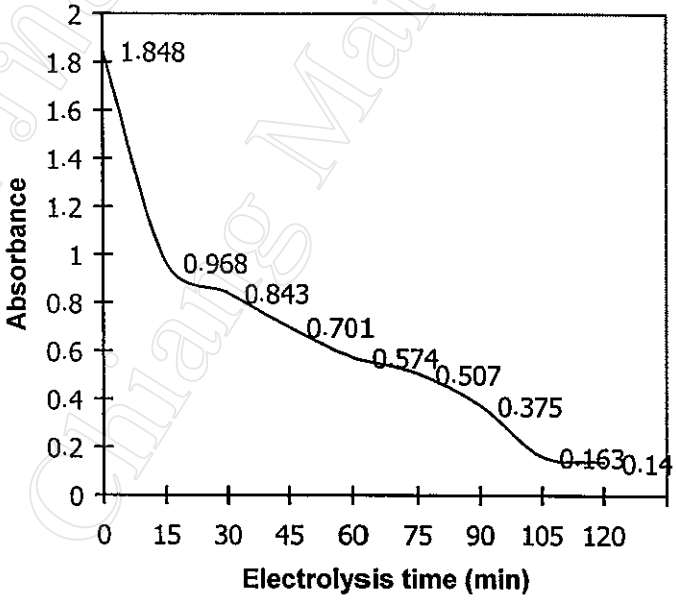


Figure 8. Plots of absorbance and electrolysis time, 0.01% w/v of morin, 262 nm



a



b

Figure 9. Plots of absorbance and electrolysis time for curcumin 0.1(*a*) and 0.2(*b*) % w/v in 5% potassium oleate aqueous solution.

The colour removal efficiency was calculated from the relative decrease of absorbance at the end of the electrocoagulation process. Figure 8 shows the

decolourization of the morin containing solution. After the electrocoagulation process, the solution was colourless and the colour removal efficiency was 100.0%. Similarly, under the same conditions 96.0% colour removal for crocin was obtained (Figure 7).

The removal efficiency for the decolourization of curcumin containing solutions in potassium oleate was 95.4% and 92.4% for 0.1% and 0.2% w/v curcumin solutions, respectively (Figure 9). It can be seen that the decolourization still shows a good removal efficiency when the concentration of curcumin increased.

The decolourization of the natural dyes was probably due to the formation of $Al(OH)_3$ in the form of gelatinous precipitate which adsorbs dyes and precipitates out of the solution. Noticeably also, dyes containing $-SO_3Na$ group seem to be coagulated readily. Understandably, this group probably reacts with Al^{3+} to form an insoluble salt.

2.3 Electrocoagulation of Phenolic Compounds

Phenolic compounds are an important class of natural products found in most parts of plants. Thus, the electrocoagulation of some phenolic compounds was studied. The electrolysis method was carried out using aluminium as electrodes. A solution of each phenolic compound (0.1% w/v) in water (1 L) was added NaCl (2g) as an electrolyte. A direct current (0.5 A, 22 V) from a DC power supplier was then passed through the solution *via* two aluminium electrodes. At 15 minutes intervals during the 2 hours period of the electrolysis, a 10 cm^3 aliquot sample of the solution was taken, and filtered. An absorbance measurement at the wavelength of the absorption maximum for each phenolic compound was as follows : phenol 250, resorcinol 272, pyrocatechol 252, pyrogallol 243, phloroglucinol 233, *n*-propyl 3,4,5-trihydroxybenzoate 243, orcinol 241, hydroquinone 243, and tannin 242 nm. The measured absorbance was then converted to the residual weight percentage of the compound by a calibration curve obtained from a plot between the absorbance versus the concentration for each compound. All of the phenolic compounds used were of standard reagent grade. The results were shown in Figure 10.

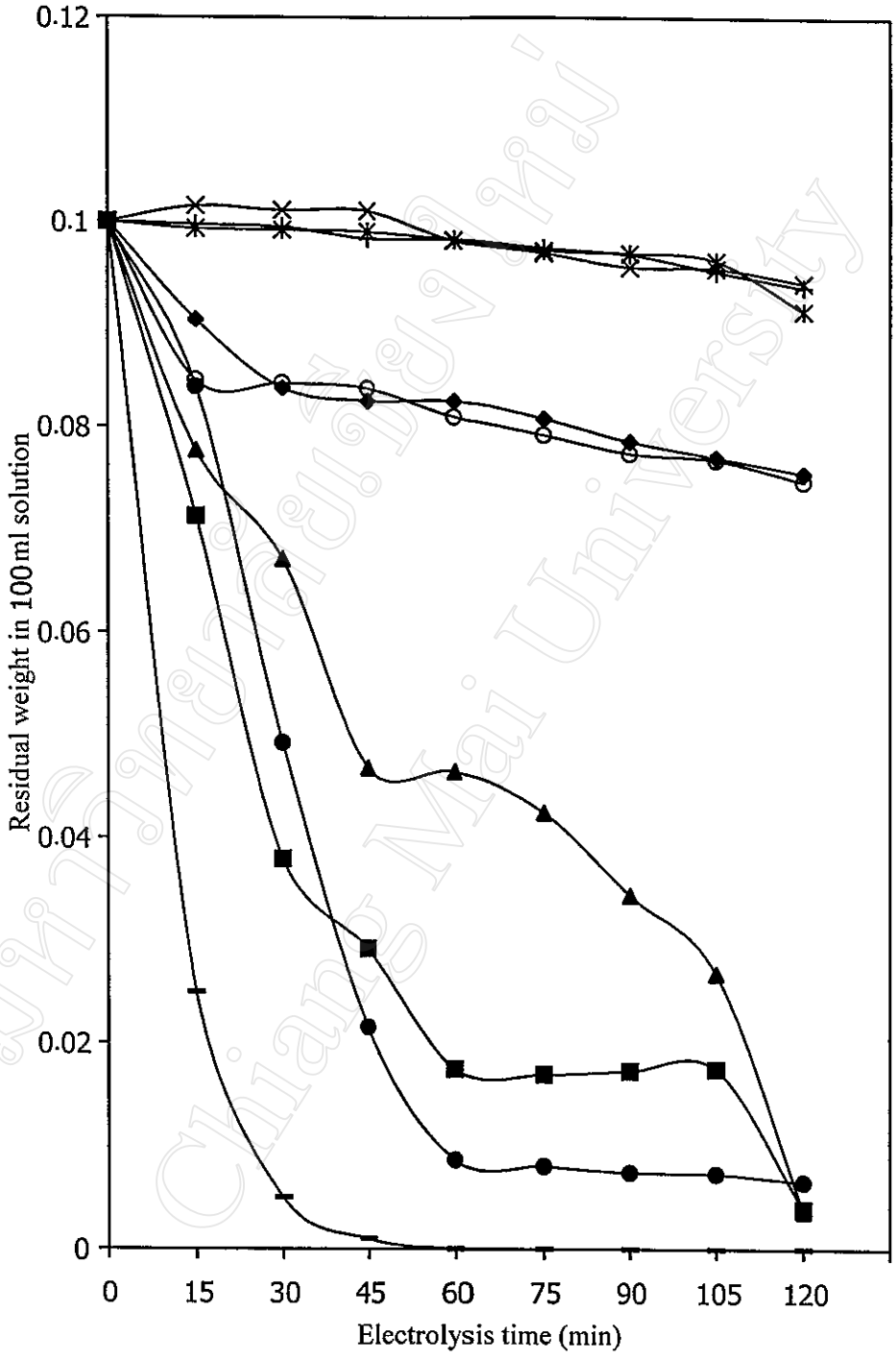
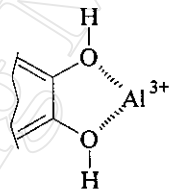


Figure 10. Plot of the residual weight percentage and electrolysis time for each phenolic compound : ✳, phenol; ◆, resorcinol; ▲, pyrocatechol; ■, pyrogallol; ×, phloroglucinol; ●, n-propyl 3,4,5-trihydroxybenzoate; +, orcinol; ○, hydroquinone; _, tannin.

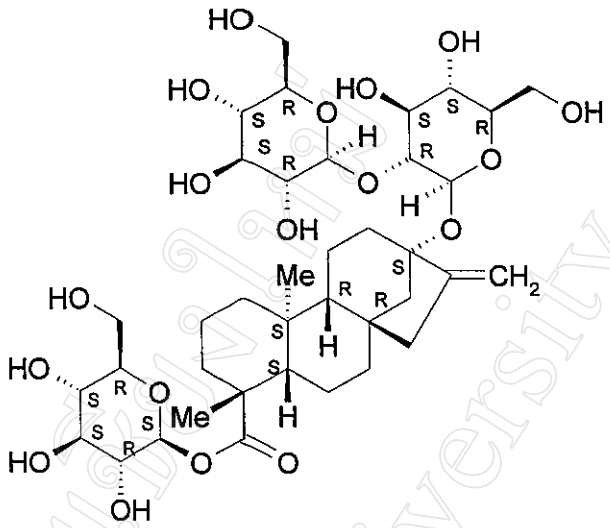
The results obtained in Figure 10 showed that there can be a degree of selectivity in complexation of the phenols with the aluminium ion, given a suitable condition, a phenomenon hitherto unreported. It can thus be seen that the phenolic compounds studied neatly fall into two categories: one stays more or less unaffected in the solution (≤8% precipitation for phenol, orcinol, and phloroglucinol, and ≤ 25 % precipitation for resorcinol and hydroquinone); another is almost completely precipitated from the solution (i.e. more than 94% precipitation for pyrocatechol, pyrogallol, *n*-propyl 3,4,5-trihydroxybenzoate, and tannin). It can thus be seen that the former category consists of phenol itself, and phenols with 1,3-dihydroxy, 1,3,5-trihydroxy, and 1,4-dihydroxy substitution patterns, while the latter category comprises phenols (including tannin) with 1,2-dihydroxy and 1,2,3-trihydroxy substitution patterns.

This suggests that the interaction of the type shown below seems to be important for preferential precipitation, even at neutral pH. This is, of course, possible only with those phenols with at least two adjacent (1,2-disubstituted) hydroxyl groups.

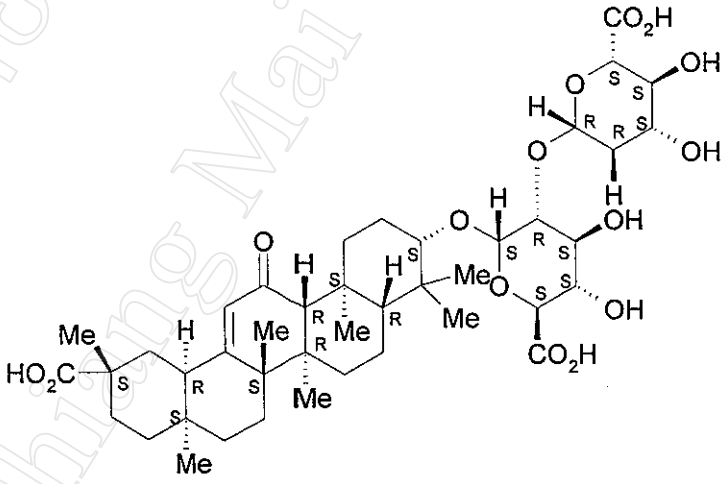


2.4 Electrocoagulation of pure glycosides

Some pure glycosides were also tested for their coagulation behaviour during the electrocoagulation process. Only glycyrrhizic acid showed a considerable degree of coagulation (Figure 13). Saponin and stevioside were unaffected (Figures 11 and 12) (The increases in absorbance, hence concentration, were probably due to solvent loss during electrolysis). Glycyrhizic acid is a glycoside that contains an acidic carboxyl group in the molecule. This probably caused it to coagulate relatively readily when encountered with Al^{3+} during electrolysis.



Stevioside



Glycyrrhizic acid

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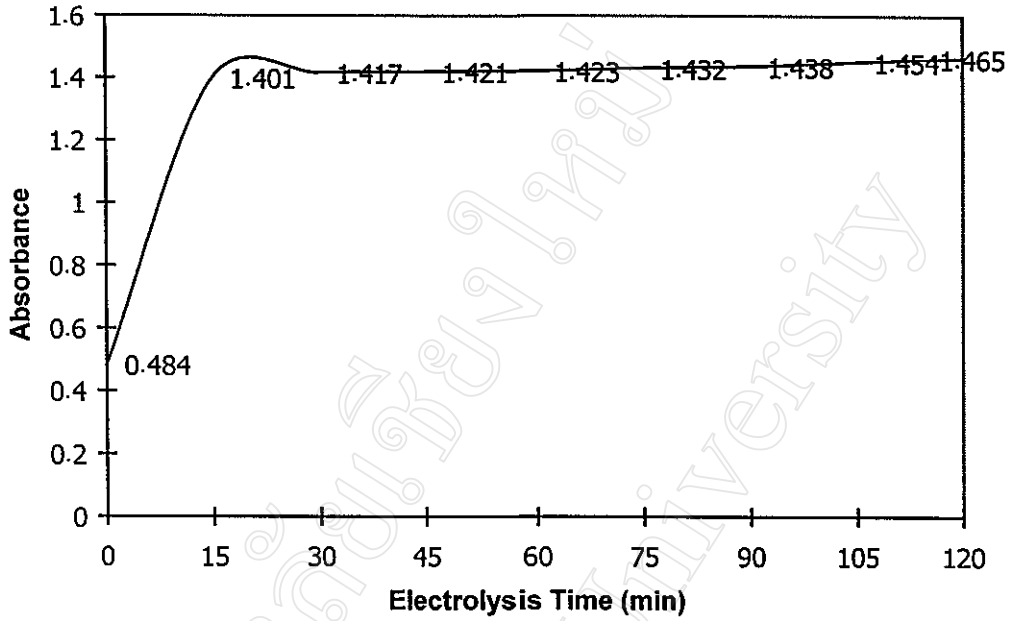

Figure 11. Plots of absorbance and electrolysis time, 0.01% w/v of saponin rein D.A.B, 194 nm

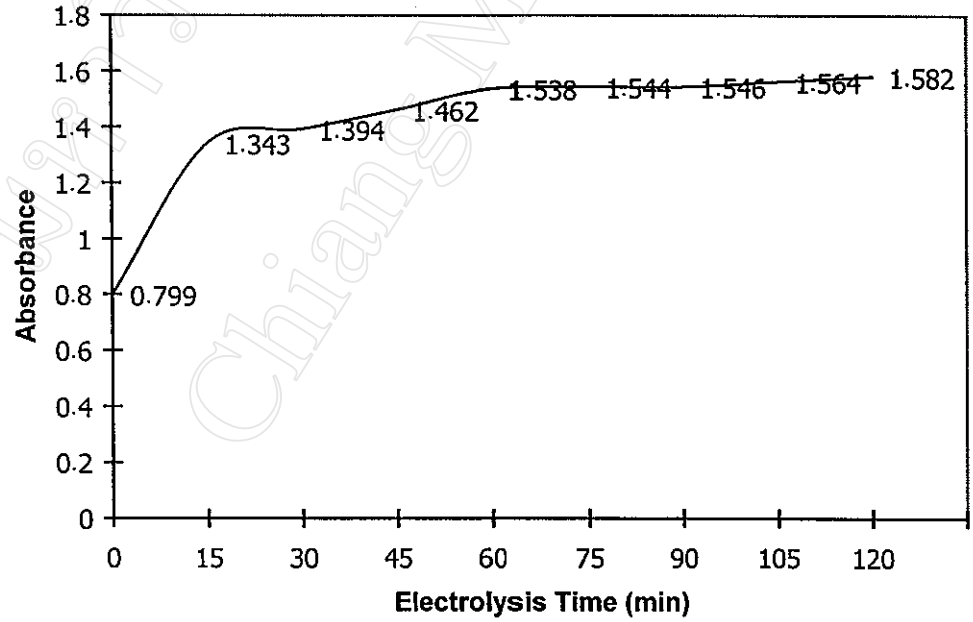

Figure 12. Plots of absorbance and electrolysis time, 0.01% w/v of stevioside, 196 nm

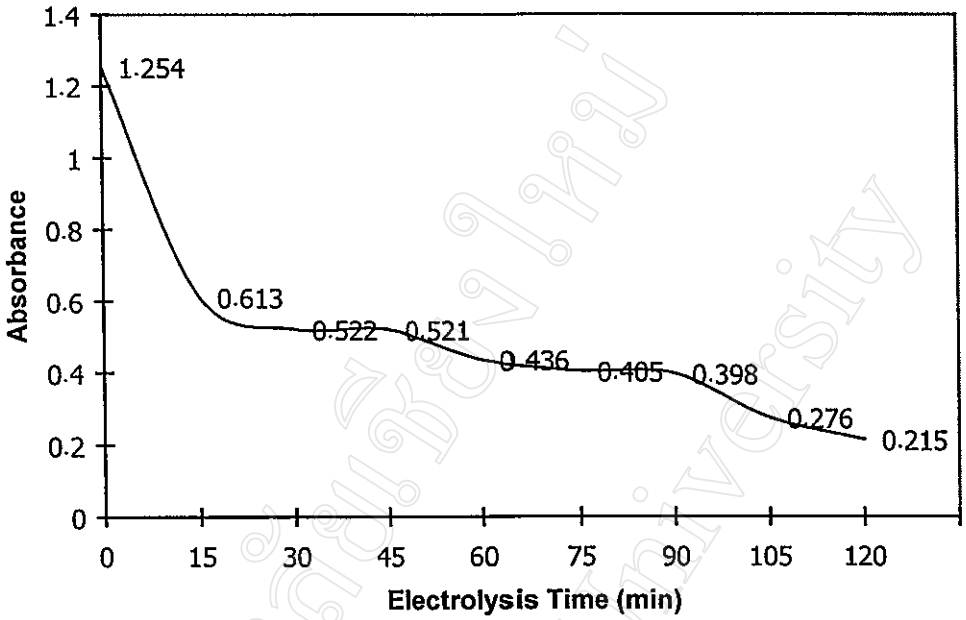

Figure 13. Plots of absorbance and electrolysis time, 0.01% w/v of glycyrrhizic acid, 256 nm

3. Model studies of electrocoagulation of chlorophyll

Since our previous model studies showed that the electrocoagulation technique provides desirable results in coagulating a number of natural and synthetic dyes, the next step is to investigate the application of electrocoagulation in removing chlorophyll, one of the ubiquitous classes of pigments found in plants. It would be of interest if chlorophyll can be removed *via* electrocoagulation method.

3.1 Electrocoagulation of standard chlorophyllin

A solution of chlorophyllin 0.01 % (w/v) in water (1 L) was added NaCl (2 g) as an electrolyte. A direct current from a DC power supplier was then passed through the solution *via* two aluminium and iron electrodes. At 15 minutes intervals during the 2 hours period of the electrolysis, a 10 cm^3 aliquot sample of the solution was taken, and filtered, and the absorbance was then measured at λ_{max} 626 nm. The absorbance

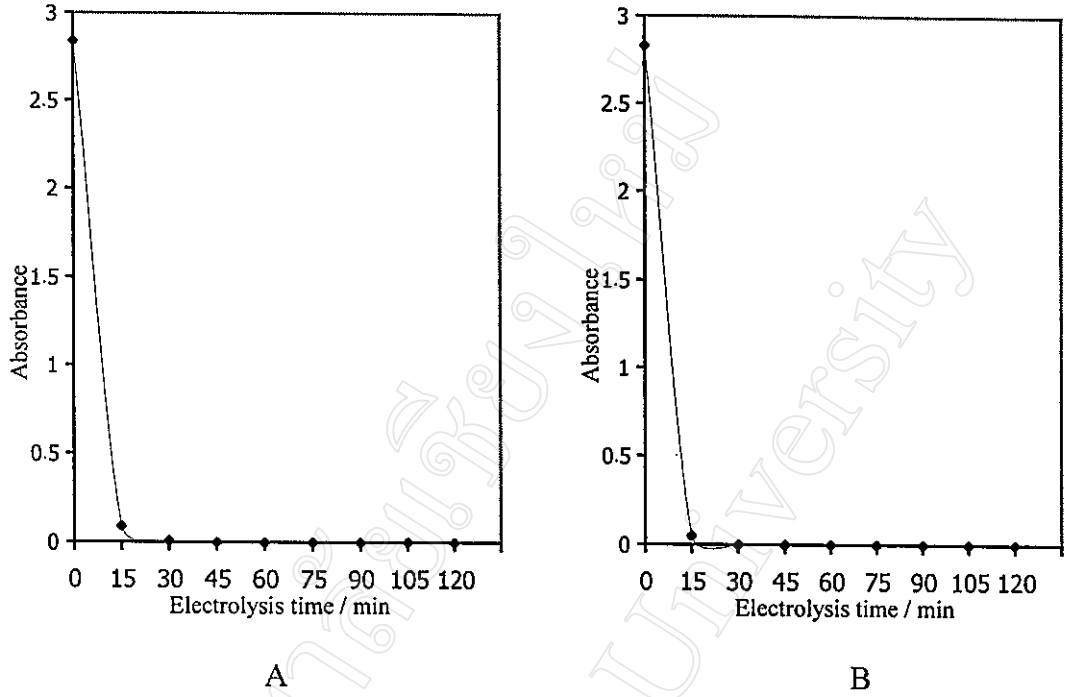

Figure 14 . Plots of absorbance and electrolysis time, 0.01% w/v of standard chlorophylline, A : aluminium electrode, B : iron electrode.

3.2 Electrocoagulation of chlorophyll from *Stevia*

Dry leaves of *Stevia* (10 g) were extracted with water (1 L). After heating at 90-100 °C for 30 minutes and then filtering, 1 litre of green solution was obtained. These solutions were then subjected to the electrocoagulation process. A solution was added NaCl (2 g) as an electrolyte. A direct current from a DC power supplier was then passed through the solution *via* two aluminium and iron electrodes. At 15 minutes intervals during the 2 hours period of the electrolysis, a 10 cm^3 aliquot sample of the solution was taken, and filtered, and the absorbance was then measurment λ_{max} 626 nm. The results also showed that chlorophyll was effectively removed with both aluminium and iron electrodes (Figure 15).

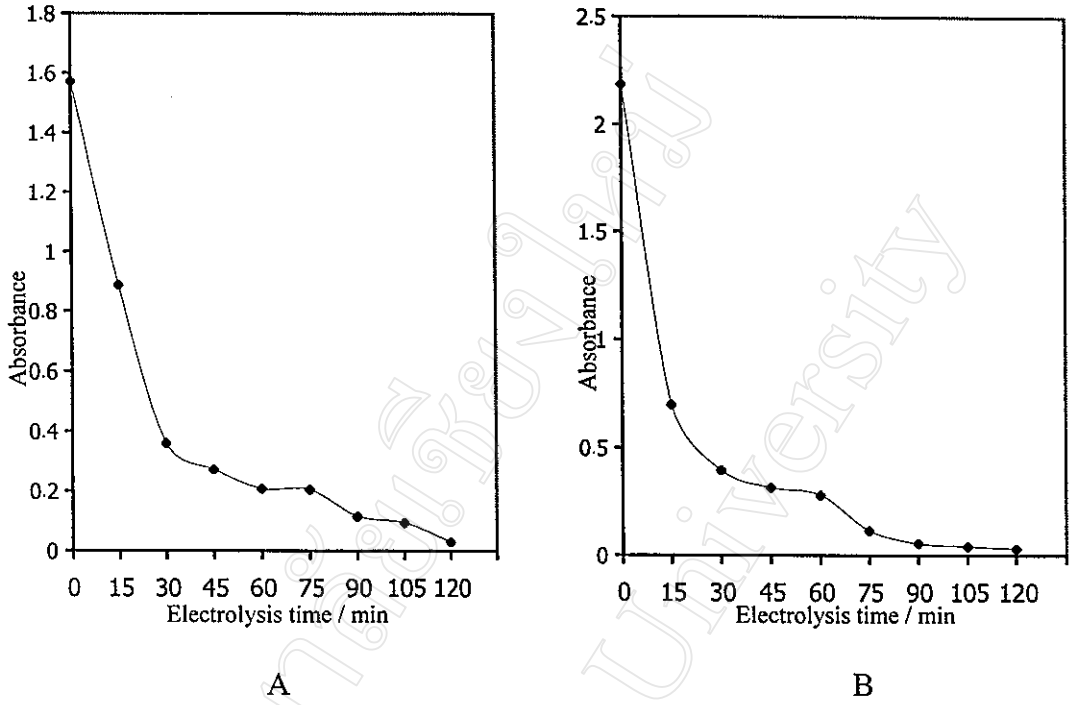

Figure 15 . Plots of absorbance and electrolysis time of *Stevia* extract, A : aluminium electrode, B : iron electrode.

3.3 Electrocoagulation of standard chlorophyllin and *stevia* extract in different ratio of water-ethanol solutions.

Chlorophyllin and *Stevia* extract solution were prepared using the same scale of the experiment described previously. The solutions (1 L each) were prepared using various ethanol/water mixtures, i.e. 100% water, 25%, 50%, and 75% ethanol in water respectively. Each solution was then subjected to the electrocoagulation process.

The efficiencies of chlorophyll elimination and the characterisation of the electrode materials were investigated. Aluminium and iron were used as sacrificial electrodes. NaCl was added as an electrolyte. An absorbance measurement was conducted at an appropriate wavelength of the absorption maximum for chlorophyll (λ_{max} 626 nm). The plots of the absorption values against electrolysis time for various concentrations of ethanol/water solution are shown in Figure 16 A and 16 B. In Figure 16 A, aluminium was used as electrodes, the results showed that standard chlorophyllin was effectively removed when only water was a solvent. The removal

efficiency dropped when the concentration of ethanol in the mixture was increased. The same was true when iron was used as electrodes (Figure 16 B). However, using Fe as electrode, electrocoagulation in 75% ethanol gave the lowest removal efficiency in case of using Fe as electrode and the electrocoagulation in 50% ethanol gave the lowest removal efficiency in case of using Al as electrode.

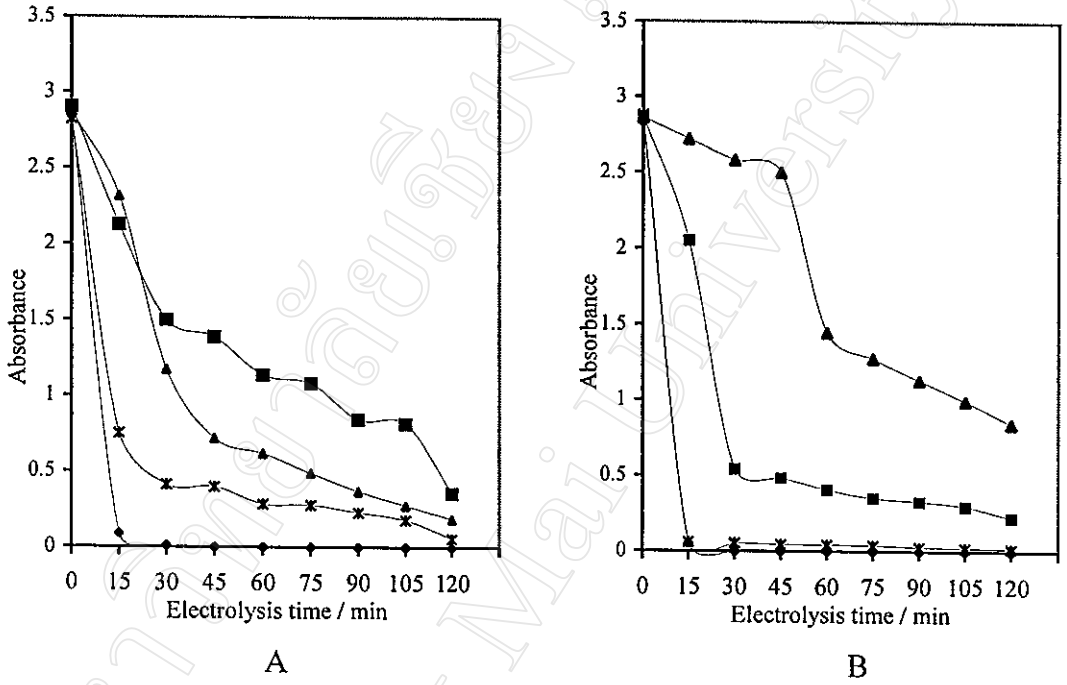

Figure 16., Plots of the absorbance value and electrolysis time for each ethanol : water ratio of chlorophyllin solution; A : Aluminium electrode, B : Iron electrode; ◆, water; ✱, 25% ethanol; ■, 50% ethanol ; ▲, 75% ethanol .

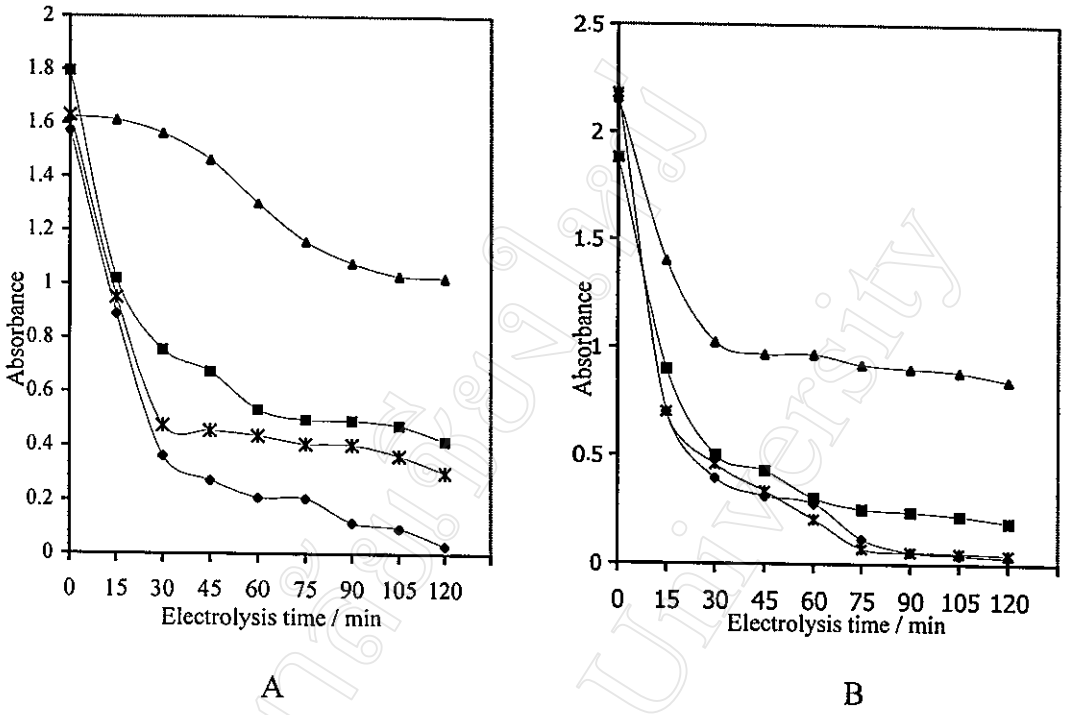

Figure 17. Plots of the absorbance value and electrolysis time for each ethanol : water ratio of *Stevia* extract; A : Aluminium electrode, B : Iron electrode; ◆, water; ✶, 25% ethanol; ■, 50% ethanol ; ▲, 75% ethanol .

The same was true for the electrocoagulation of *Stevia* extract shown in Figure 17. Chlorophyll was effectively removed from the solutions after electrocoagulation using Al as electrode (Figure 17 A). However, the removal efficiency of the electrocoagulation using the Fe electrode was slightly higher (Figure 17 B). In both case, it seems that when the ethanol concentration reaches 75%, decolourization efficiency drops dramatically. Between 0-50% ethanol concentration, however, decolourization of the pigment by electrolysis seems to be useful. During the electrocoagulation process, the electrical current dropped when the percentage of ethanol increased (as shown Table 2). Due to the limitation of the power supply, the current could not be increased to the initial 2 ampere. This might be one of the reasons why the removal efficiency decreased when the concentration of ethanol increased.

Table 2. Electric current values during electrolysis of each extraction.

Electrodes	Al or Fe	
	Current (ampere)	Voltage
100% water	2	20
25% ethanol	1.4-1.8	20
50% ethanol	0.8-1.8	20
75% ethanol	0.5-0.8	20

The average yields of crude stevioside obtained with Al and Fe elctrodes were 9.1% and 4.16 % respectively (Lit[8]. 7-10% yield using Al electrodes). The result shows that although pigment removal efficiency of the electrocoagulation using Fe electrode was slightly higher than Al electrode, it also has an adverse effect to the yield of the desired glycoside.

4. Conclusion

Aqueous solutions of certain synthetic and natural dyes and pigments including chlorophyll, and also solutions of certain phenolic compounds including tannin can be electrolytically decolourized by the process of electrocoagulation. In the case of an alcoholic solution of chlorophyll and related pigments, electrocoagulation can still be of some use for decolourization up to an alcoholic concentration of 50%. Some glycosides studied were unaffected by electrocoagulation, hence warranting further investigation of the use of electrocoagulation as a general method of isolation and purification of glycosides from natural source.

5. Experimental

General procedures

Absorbances were recorded on Perkin-Elmer UV Vis spectrometer.

Leaves of the plant, *Stevia*, were supplied by Dr. Veruree Srithep, Chiang Mai University.

All of the chemicals used were of standard reagent grade.

Electrocoagulation procedures

Two aluminium plates or two iron plates (dimension 30 x 10 x 0.05 cm) were used as electrodes. These were dipped 3 cm apart and 9 cm deep into a magnetically-stirred aqueous solution (1 litre) in a glass jar (diameter 11 cm, height 23 cm). Sodium chloride (2 g) was added as an electrolyte. Direct current (0.5 A, 22 V) from a DC power supplier was then passed through the solution *via* the two electrodes. At every 15-min interval during a 2-h period of electrolysis, a 10-cm^3 aliquot sample of the solution was withdrawn, filtered, and taken for an absorbance measurement at the wavelength of the absorption maximum for each compound.

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