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Technical Revival of Traditional Blue Dyeing through Zeolite Catalysis and Electrolysis

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關 鍵 字： **Zeolite、Indigo Dye、Electrolysis**

作者介紹

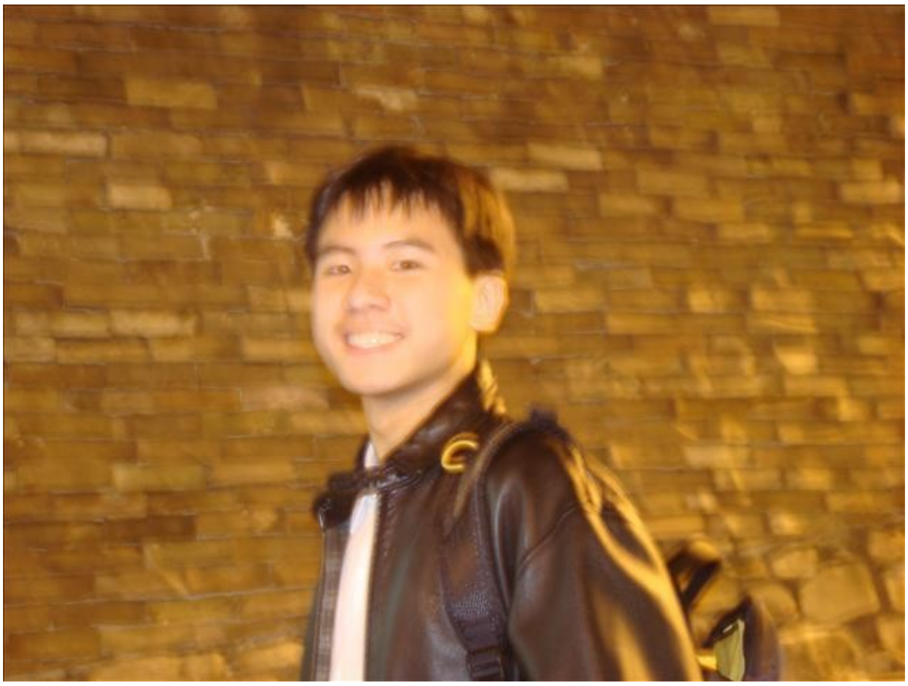
大家好，我是曾翰柏，現在就讀台南一中一年級，自小便對科學抱持著很多憧憬，是一個抱著”目擊者(Eyewitness)”系列叢書長大的小孩。很高興能藉由參與此次的科展發展自己的興趣並增進學習的機會，也認識許多志同道合的青年!

做此次科展之初，我甚至還沒入學，還只是一個剛考完國中基測，對高中生活與國際科展一無所知的”中中生”，卻被化學老師 SD 和學長抓來做科展!!起初，我真的是做得一頭霧水，畢竟國中的知識往往不能勝任老師和學長提出的理論，讓自以為基測高分的我深受打擊!但也因此，我才在這一次的科展中學到這麼多。

這次做的科展是以傳統的染布技術的環保化及工業化為研究重點。畢竟這是台灣祖傳百年的傳統產業，再加上我自己是半個客家人，所以我對於藍衫文化感到額外親切。這次除了非常想要將這個優良的傳統產業變得更加優良，更想將之以”台灣產業”的名義，在國際上發揚光大，讓世界人人都認識台灣!!

在這次的科展活動中可能做到這個地步，學習到這麼多，當然要感謝一邊考學測一邊做科展的學長、辛苦指導我們的老師、全力支持我父母，還有很多很多人!! 謝謝大家!!

作者介紹



我是洪仲凱，目前就讀國立台南一中高三數理資優班。從小由於興趣廣泛，參與許多各方面的活動以及比賽，包含體育、音樂、棋藝、科學等。除了平時習慣閱讀科普資料外，寒暑假亦會參與科學相關的營隊，如去年暑假的 TTSA 高中物理營。在語文方面，我曾代表學校參加全國性的比賽，如 2007 外交小尖兵。去年六月更代表台灣赴莫斯科參訪。在學校社團則是擔任劍道社社長，曾辦過台南市的比賽。

高二下時，我接觸了台灣傳統的藍染工業，在進一步的了解後，看見其潛力，因而投入此研究。在研究過程，我除了深入了解了傳統藍染工業，更學習到科學研究的方法以及處理問題的能力。

Abstract

This study aims to improve the reduction process of Traditional Blue Dyeing and tackle its problems of inefficiency, air and water pollution, and waste disposal. The world today craves for natural, eco-friendly products. Our project provides an efficient process by which the traditional method of dyeing blue cloth with natural Indigo Dye, which used to be time-consuming, inefficient, and highly polluting, can be revived in an efficient and eco-friendly way.

We found out from records that the reduction of Indigo Dye into Leuco Indigo is the process which causes the greatest pollution. This project utilizes Pt-Zeolite to catalyze the reduction of Indigo Dye into Leuco Indigo for dyeing cloth, because of the porous structure of zeolite and the catalyst effects of Platinum. The zeolite catalysts were sintered onto pieces of argil at temperatures 450~600 ℃. The argil held together the otherwise powder-form catalysts throughout the reaction, relieving its operators from the otherwise unnecessary task of filtering the catalysts every time after reaction. Argil's characteristics of malleability and reusability further promise high practical use.

Further improvement was achieved with electrolysis, which successfully reduced cost and greatly simplified production. Moreover, electrolysis replaced the original need for gas-form hydrogen, making the process cheaper and safer. Compared with the traditional process, electrolysis achieved much higher efficiency and speed, taking only two hours to produce enough Leuco Indigo for dyeing, while the traditional method takes a matter of weeks. In comparison to the chemical process, electrolysis is more eco-friendly, using less chemical compounds.

Washing blue fabrics after dyeing produces waste fluids with low concentrations of Indigo Dye. Hence, we came up with a process by which waste materials can be oxidized into harmless gases. Through the use of Fe-zeolite and free radicals produced on the anode of the electrolysis apparatus, we succeeded in oxidizing all waste Indigo Dye into completely harmless water and carbon dioxide using the lowest cost possible.

This improved procedure has not only overcome the disadvantages of traditional blue dyeing but also preserved its natural characteristics. Therefore, we believe that this procedure has high industrialization potential and will bring to the world a great new choice of eco-friendly products.

中文摘要

在環保意識抬頭的今日世界，人們尋求一切辦法找出兼具環保與工業價值的產品與製程。我們的實驗正是以此為研究宗旨，融合傳統的藍染工業，希望能復甦使用天然染料的藍染工業。由於靛藍是不溶於水的染料，在染布前必須先將它還原成靛白隱色鹽才能使其附著在布料上。靛藍的還原不僅是藍染的重要步驟，更會直接影響到染布的品質，但傳統藍染所使用的生物發酵還原過程既耗時、耗損染料也造成極度空氣及水污染，因此本實驗決定研究其改善之道。

基於沸石多孔、大表面積等特性，以及金屬鉑擅於催化的特性，我們決定以這兩種東西的結合—鉑黑沸石，來催化靛藍的還原。為了防止粉末狀的鉑黑沸石在靛藍廢液的排放中流失，甚至造成污染，我們將它燒結於陶土塊上，在實驗中探討最佳的燒結溫度，並得知為 450~600 ℃。陶土不只能定住沸石，還具有高可塑性，工業上能將之設計成任何形狀，並且能夠重複使用，故此法極具工業價值。

在成功的以鉑黑沸石陶土催化反應之後，我們更進一步嘗試用電解來提高反應的效率，且效果十分良好。傳統的還原過程所需時間長達 2、3 個禮拜，且因為使用生物發酵法，十分耗能。相較於傳統生物發酵法，電解法能源效率高，比傳統法更快，只需要反應 2 個小時即可達到良好的染布效果。至於使用還原劑的化學法，電解法雖然未如其迅速，卻有容易操縱、能源效率高、無污染性產物或原料、及成本低等優點，在商業及環保考量上，是實質的勝出了。

本研究更進一步的探討廢液處理的問題，並成功的使用一樣可以重複使用的鐵沸石陶土配合在電解裝置正極所產生的自由基成功以低成本將剩餘的廢液完全氧化為二氧化碳及水。

本研究成功地提供一個完整的工業程序，賦與天然藍染全新的生命。

Technical Revival Of Traditional Blue Dyeing Through Zeolite Catalysis and Electrolysis

1. Introduction

Ever since the Qing Dynasty a method of dyeing cloth with Indigo—a natural plant extract—has been practiced in Taiwan and southeastern China, producing large amounts of beautifully dyed blue traditional clothing. Yet this traditional technique, being dye-wasteful, time-consuming, environmentally unfriendly, was lost in the heat of industrialization, having been replaced by chemical processes, which were fast, cheap, but harmful to both the environment and humans. Thus in the modern era of natural products and environmental awareness, we saw the need for the revival of this traditional technique--not just to restore it the way it was, but to make it faster, cheaper, and more environmentally friendly than ever.

The dyeing of cloth with Indigo Dye depends greatly on the reduction of Indigo Dye into Leuco Indigo, a clear, slightly yellow, and water-dissolvable substance that coheres onto the cloth with much more efficiency than Indigo Dye itself, which is non-water-dissolvable. Thus the traditional process utilizes biofermentation, which reduces Indigo with microorganisms. Though this process successfully transforms Indigo Dye into Leuco Indigo, the transformation rates are extremely low. Also, as it uses microorganisms, the traditional process is also energy consuming and hard to manage, requiring continuous care, agreeable temperature and humidity. The utilization of biofermentation has another defect; the strongly unpleasant smell released into the air of the vicinity caused the local Taiwanese to call the blue dyeing workshops "Chou-sai-hug," meaning "Blue Cesspit." Also, the traditional process, low in reduction rates and operated in an open system in which the reduced Leuco Indigo oxidizes back into Indigo Dye, produces large amounts of unrecyclable waste fluids, polluting rivers and lakes.

The dyeing of cloth with Indigo is composed of three stages: (1) The fermenting of Indigofera plants for Indigo Dye; (2) Reduction of the non-water-dissolvable Indigo Dye into water-dissolvable Leuco Indigo; (3) Dyeing and airing (oxidization) the cloth. The reduction process is key to the efficiency and final quality of blue dyeing. The dyeing method commonly used today heats the raw material to fix the dye onto cloths; yet the heating decreases raw material and energy efficiency. Our project provides a faster, cleaner process for the reduction of Indigo Dye by using Pt-Zeolite as a catalyst, mixed and sintered with Argil, which gives the resulting "Pt-Zeolite Argil" high malleability, and therefore high practical use. The best sintering temperatures were also examined through experiments.

As the reaction required hydrogen, we first added hydrogen reacted from hydrochloride and zinc. Then, considering the cost and operation of production, we came up with the idea of using electrolysis to produce hydrogen instead, which is both cheaper and safer to operate than hydrogen gases. The reduction reaction's being performed in electrolyte solutions make it even more suitable for the industrial application of electrolysis. Through experiments and discussion we found that the amperage of electricity, the concentration of Indigo Dye and the size and shape of the Pt-zeolite argil all affect the rate and efficiency of the reduction.

To completely eliminate the problem of environmental pollution seen in both the traditional method and today's common practices, we used "Doping Fe-Zeolite," also sintered with Argil, to catalyze the oxidization of waste fluids, and successfully converted all waste matter from Indigo Dye into CO_2 and H_2O.

Finally, we improved the reduction process of blue dyeing and eliminated its original problems of pollution and waste disposal.

2. Objectives

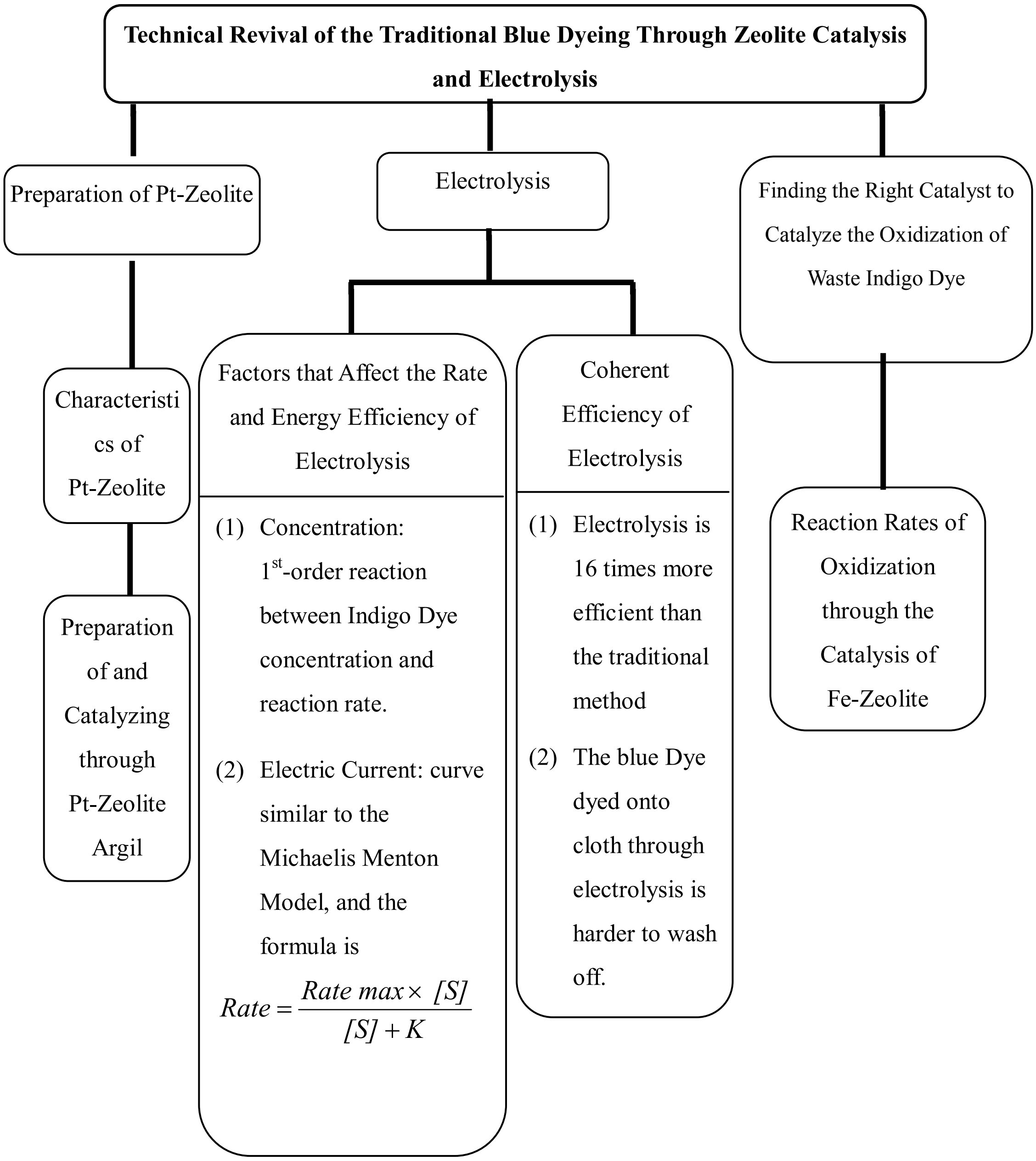
(1) To increase energy efficiency, reaction rate, and cost-efficacy of Blue Dyeing through self-made zeolite catalysis and electrolysis.

(2) To reduce the pollution, cost and operative complexity of Blue Dyeing through the practical use of self-made zeolite catalysis and electrolysis.

(3) To revive the method of dyeing cloth with natural Indigo Dye, and make it more eco-friendly than ever before.

(4) To discuss future use of zeolite catalysis and electrolysis in the dyeing industry.

3. Experiments



3.1 Preparation and Analysis of Pt-zeolite

Two solutions of sodium silicate and sodium aluminate in sodium hydroxide were prepared and mixed to form a gel-form solution, which was stirred until even. Then the gel solution was then put in a PP bottle and sealed inside. The bottle was heated in water to 90~100℃ for 4 hours, and then left at room temperature to cool. The heated gel solution was vacuum-filtered, and “washed” with distilled water until its pH was 9. The vacuumed remains of the gel (blank zeolite) was then dried in a furnace at 100~120℃. A solution of 5 mM $PtCl_4$ was added to the blank zeolite and sintered at 125℃ for 15 minutes to make Pt-zeolite. The Pt-zeolites were then scanned with SEM to analyze its surface characteristics.

The same procedure was also used to make the Pt-mica used in later experiments.

3.2 Catalysis of Indigo Dye Through the Use of Pt-zeolite

3.2.1 Catalysis Efficiency of Pt-zeolite, Pt-embedded Mica, and Pure Zeolite

An Indigo Dye solution of 1/3 relative concentration was put inside a syringe with Pt-zeolites (0.5 g) and H_2 (10 ml) to react. The syringe was then shaken and photographed every 30 seconds. Finally the transparency of the solutions in the photos were analyzed, the reaction curves drawn, and the reaction rate calculated from the slope. The experiment was repeated with Pt-mica and pure low-silicon zeolite as catalysts, respectively, in order to determine the working catalyst in the reduction of Indigo Dye. (Appendix picture 1., picture 2.)

3.2.2 Preparation of Pt-zeolite Argil

The same amounts of Pt-embedded zeolite and dried argil powder were mixed together, then mixed with water. The mixture was then shaped, air dried, and sintered in the furnace. The catalysts' effect was determined by the catalyst's efficiency in catalyzing the decomposition of hydrogen peroxide, producing O_2, which was measured with a pressure sensor.

3.2.3 Catalyzing with Self-made Pt-zeolite Argil

A closed system was designed for Indigo Dye to be reduced into Leuco Indigo without exposure to air (Figure 1., Appendix picture 3.). First, an adequate amount of hydrogen was put into Syringe A, after which Pt-zeolite Argil and Indigo Dye were put into Syringe B. Then, Syringe A and Syringe B were connected with a three-way stopcock, providing a passage for hydrogen to enter Syringe B. Finally, hydrogen was pushed into Syringe B and sealed inside to react.

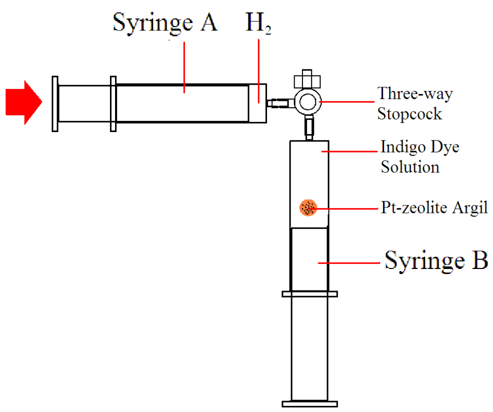


Figure 1. The closed reduction system.

3.3 Electrolysis

An innovatively designed electrolysis tank (Figure 2.) and a programmable linear power supply system were used in these experiments to supply electric currents for the reduction of Indigo Dye. The tank was separated into two cells by a semi-permeable membrane. One cell was filled with an Indigo Dye-KOH solution. A catalyst-electrode was connected to the negative pole of the power supply and placed at the bottom of the Indigo Dye-KOH cell to produce H_2 and catalyze the reaction. The catalyst-electrode also acted as an agitator, as hydrogen bubbles mixed the solution as they rose to the surface. The other cell was filled with a KOH solution; a platinum electrode was inserted into the KOH cell and connected to the positive pole of the power supply.

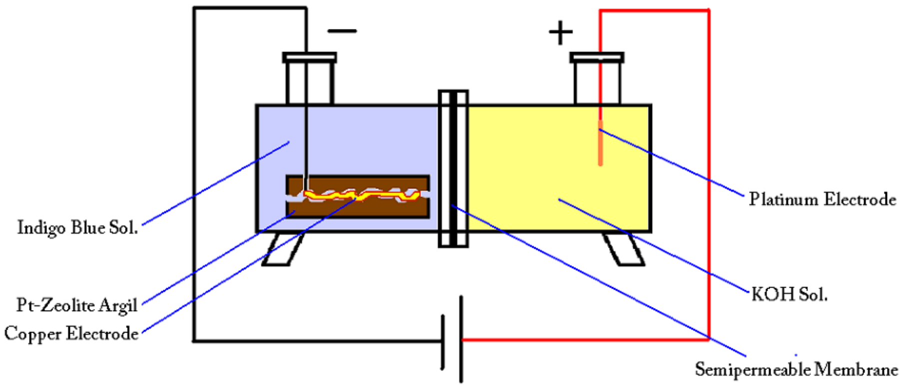


Figure 2. The self-designed electrolysis tank and power system.

3.3.1 Measuring Indigo Dye Concentrations

In the following experiments (3.3.2 and 3.3.3), the concentration of Indigo Dye in the solutions were measured by adding an excessive amount of sodium borohydride solution (Solution A) to Indigo Dye solutions to reduce Indigo Dye into Leuco Indigo; then the solutions were added into a hydrochloride solution to let the extra sodium borohydride react with hydrochloride into H_2. Then the volume of H_2 was recorded and compared with that of H_2 produced from unused Solution A and hydrochloride. (Figure 3.) Thus, from the difference of the amount of $NaBH_4$, the moles of the Indigo Dye in the solution could be calculated

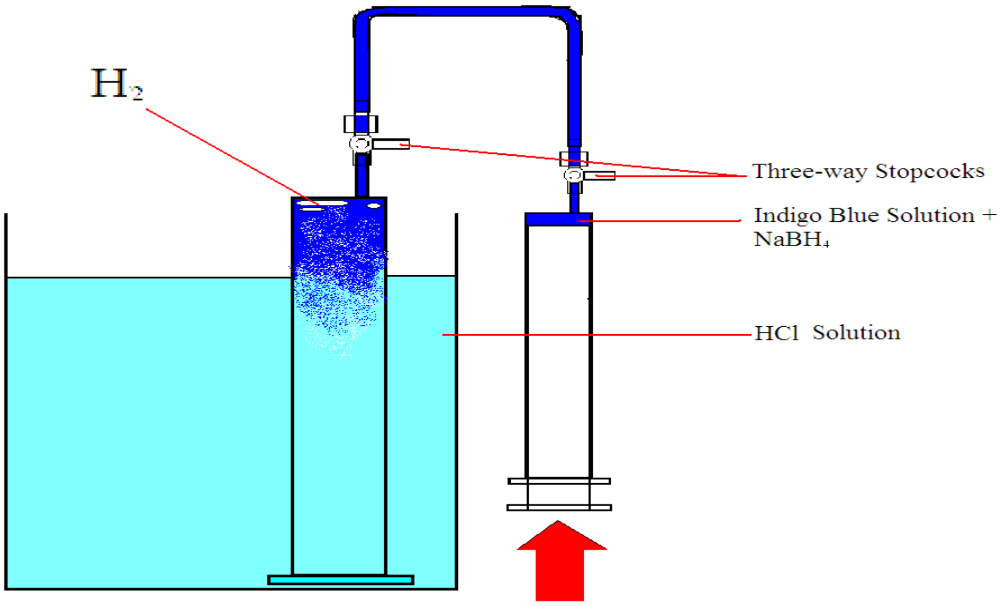


Figure 3. The self-designed apparatus used to measure Indigo Dye concentrations.

3.3.2 Effects of Concentration on the Reduction of Indigo Dye

In this experiment, the effects of different Indigo Dye concentrations on the reduction of Indigo Dye were examined by putting Indigo Dye solutions of different concentrations (0.05 M~0.25 M) separately into the electrolysis tank with an electric current of 1.0A applied for 1 hour. The reaction rates of these different solutions were calculated by comparing the Indigo Dye concentration differences in these solutions. Concentrations were measured as described in 3.3.1.

3.3.3 Effects of Electric Currents on the Reduction of Indigo Dye

In this experiment the effects of different electric currents on the reduction of Indigo Dye were examined by applying different electric currents (0.5 A~2.5 A) to Indigo Dye solutions of the same concentration (0.2 M) in the electrolysis tank for 1 hour. The reaction rates of the reduction in these solutions were measured and the calibrated curve of Current-Reaction rates drawn.

3.3.4 The Comparison of the Indigo Dye Coherence Efficiency of the Traditional Method and the Electrolysis Method

The purpose of this experiment is to compare the efficiency of the traditional method and the electrolysis method through the measurement of the amount of Indigo Dye cohered onto the cloth. In this experiment, two pieces of gauze (1.052 g/each) were dyed, one heating in Indigo Dye water at 70℃, and the other wrapped around the Pt-zeolite argil in the electrolysis tank (Figure 4.). The concentration of Indigo Dye used in this experiment was 0.21 M, and the electric current applied to the electrolysis tank was 2.0 A, the lowest speculated current for the maximum reaction rate. The reaction time was 2 hours. After this, the amount of Indigo Dye on the cloths was measured.

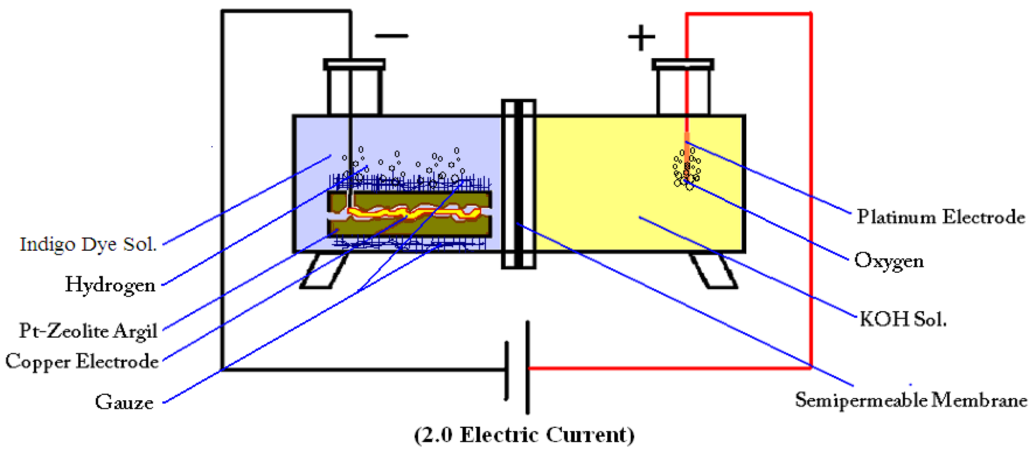


Figure 4. The self-designed apparatus to measure the Indigo dye coherence efficiency.

3.3.5 Comparing Color Fade of Cloth Dyed Through the Traditional Method and the Electrolysis Method

Because the quality of the reduction has immediate effect on the quality of dyeing, another experiment on the comparison of the dyeing results of the traditional method and the electrolysis method was conducted. The main difference of this experiment from that in 3.3.4 is that in this experiment the degree of color reduced (color fade), rather than cohered, was the main measurement according to which the experiment was concluded. This time the gauze used in the traditional method was heated for 16.5 hours in the dyeing process; the electrolysis method used to dye the other piece of gauze was performed as in 3.3.4. After this both of the cloths were dried, heated in 50℃ water for 5 minutes, and photographed to analyze and graph the difference in color fade through PhotoImpact 7. This step was repeated for four times (Appendix pictures).

3.4 Disposal of Waste Indigo Dye by Using Fe-Zeolite Argil

3.4.1 Preparation of Fe-zeolite

The Fe-zeolite argil was made in two ways: ion-exchange and hydrothermal synthesis. In the former procedure, the zeolite was soaked in a 0.6 M Ferric Nitrate solution, then cleansed, and finally sintered in a furnace. In the latter, the Fe-zeolite was made though a homogeneous reaction by bathing $Fe(NO_3)_3$ and silicate in alkaline solution prepared by mixing sodium hydroxide (NaOH) with an appropriate amount of water, and heated for 4, 8, 12, 24 hours, respectively. Afterwards, the catalysis rates of the five zeolites, $Fe(NO_3)_3$, and Fe_2O_3 in the decomposition of peroxide were compared with a pressure analysis apparatus.

3.4.2 The Reaction Rate of Fe-zeolite Argil Anode in Catalyzing the Oxidization of Indigo Dye

The purpose of this experiment is to measure the oxidization rates of Indigo Dye waste fluids through the catalysis of Fe-zeolite with free radicals produced in the electrolysis tank's anode. In this experiment a Fe-Zeolite embedded Argil was attached to the anode of the electrolysis tank, to catalyze the oxidization of waste fluids. First, an Indigo Dye solution of 0.006M concentration was prepared and put in the anode of the electrolysis tank. An electric current of 0.05A was applied, and the concentration of the waste fluids

(Indigo Dye) was measured with a spectrometer (Hitachi U-2001) every 10 minutes, and the energy efficiency calculated.

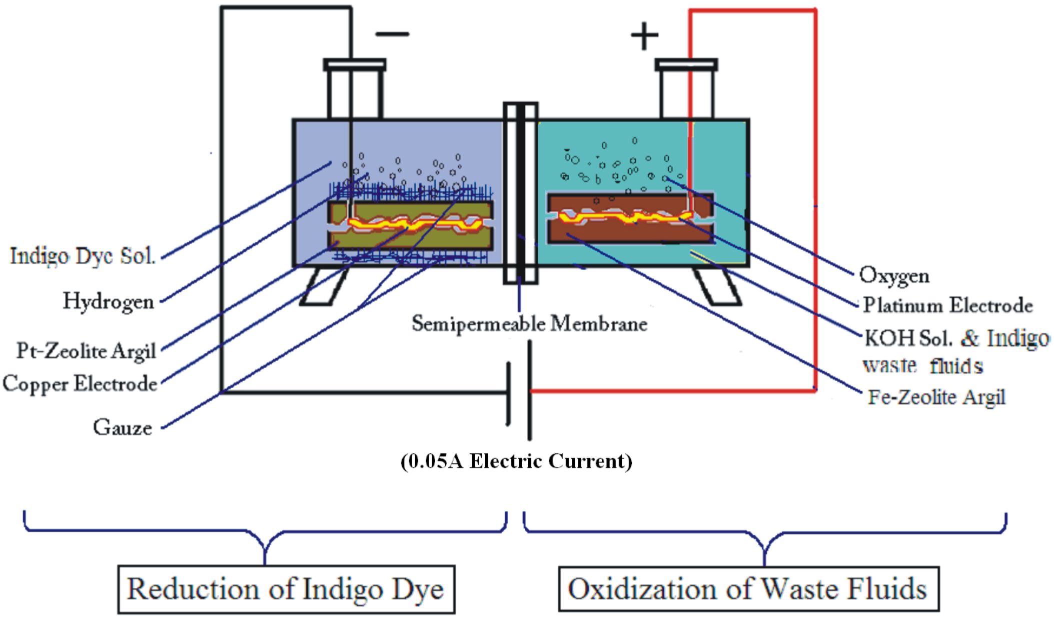


Figure 5. The Indigo reduction and oxidization combined apparatus.

4. Results and Discussion

4.1 Preparation and Analysis of Pt-zeolite

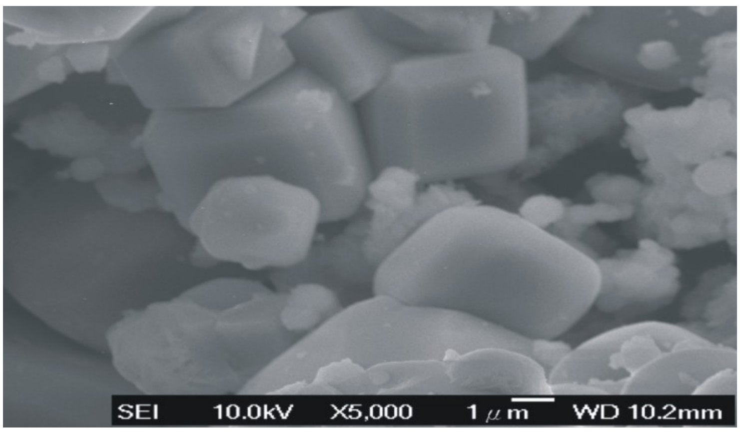


Figure 6. SEM image of the catalyst (Pt-Na-Al -SiO2) calcined at 398 K.

SEM image of Pt-zeolite sintered at 623 K shows cubic Na-Al -SiO_2 crystals and small nano-colonies of Pt attached onto the zeolite. The structure of the zeolite has a visibly high surface area, an ideal coherent material for the nano-Pt catalyst.

4.2 Catalysis of Indigo Dye through the use of Pt-zeolite

4.2.1 Catalysis Efficiency of Pt-Zeolite, Pt-Mica, and Pure Zeolite

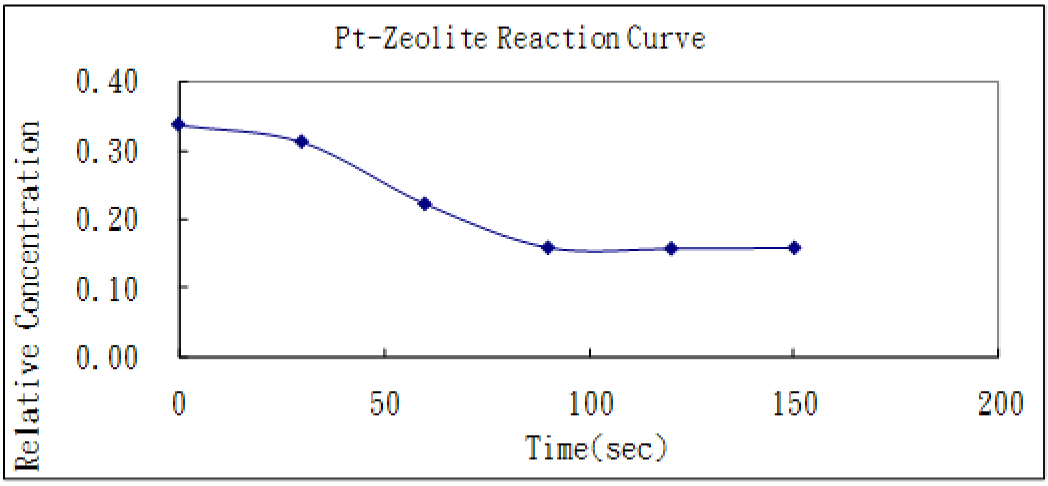


Figure 7. Pt-zeolite reaction curve.

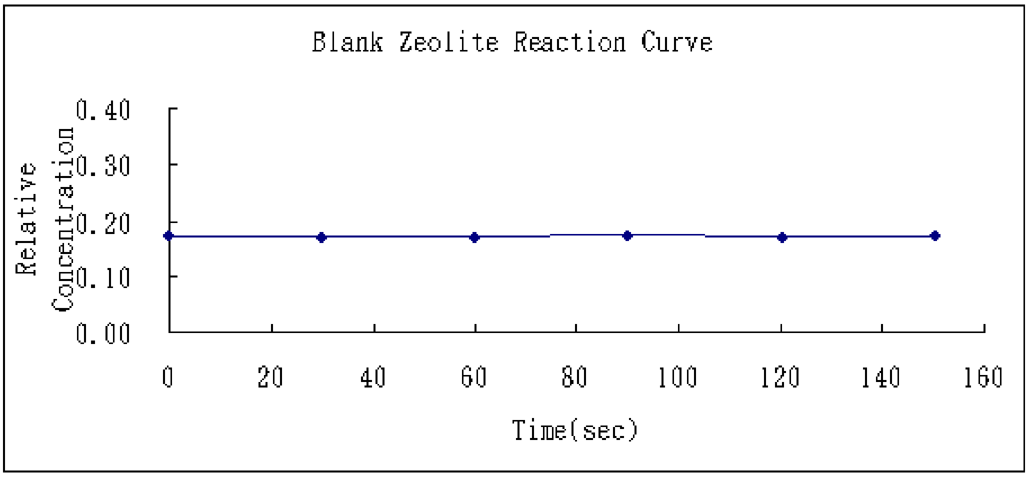


Figure 8. Blank zeolite reaction curve.

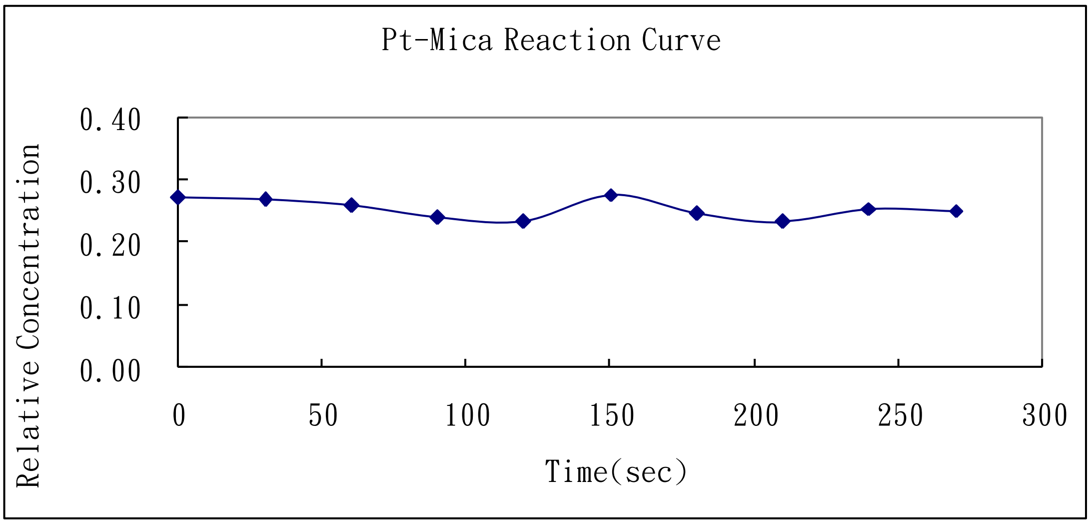


Figure 9.　Pt-mica reaction curve.

Table 1.　Comparison of reaction rates.

Zeolite	Pt-zeolite	Pt-Mica	Blank zeolite
Slope	0.00209	0.00000	0.00000

Although minor fluctuations in relative concentration in the reaction with Pt-mica were recorded, they were presumed to be light reflecting off the Mica plates and considered insignificant, as no visible color differences were observed. Pure Zeolite did not react with Indigo Dye, either. (see pictures in Appendix). Thus it was proved that the working catalyst in the reduction of Indigo Dye is Pt-zeolite, not Pt or zeolite alone. Mica was used as a coherent for Pt, and did not react in or catalyze the reaction.

4.2.2　　Preparation of Pt-zeolite Argil

Pt-embedded zeolite argil sintered above 450°C was best at catalyzing hydrogen peroxide, yet temperatures above 600°C caused a flatten sheet of zeolite to form on the argil, resulting in zeolite having too little a surface area to be efficient in catalyzing

H_2O_2. Thus the best sintering temperature was concluded to be between 450°C and 600°C.

4.2.3 Catalyzing with Self-Made Pt-Zeolite Argil

The product solution of this experiment was yellow in color, and turned blue after being exposed to air, showing that the product is indeed Leuco Indigo. This proves that Pt-zeolite Argil does have the ability to reduce Indigo Dye into Leuco Indigo.

4.3 Electrolysis

4.3.1 Method of Measuring Indigo Dye Concentration with $NaBH_4$

Through analysis of the structure of Indigo Dye known from some archives, it was calculated 1 mole of Indigo Dye required 1 mole of hydrogen to reduce (N_{H2}=N_{indigo}). Thus the following formula explains the calculation of Indigo Dye concentration ($C_{M(indigo)}$) from the amount of hydrogen produced (V_{H2}).

$$C_{M(indigo)} = \frac{PV_{H_2}}{RT} \times \frac{1000}{110mL}$$

4.3.2 Effect of Concentration on the Reduction of Indigo Dye

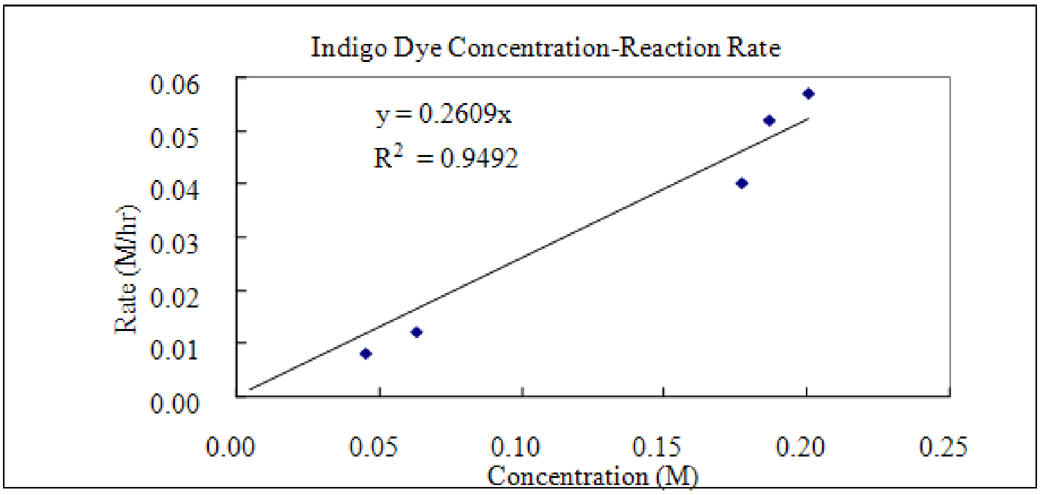


Figure 10. Indigo dye concentration-Reaction rate.

The effect of the concentration of Indigo Dye shows a linear curve (1st-order reaction). Thus it can be seen that the concentration of Indigo Dye in the solution has direct and easily manageable impact on the rate of the reaction.

4.3.3 Effects of Electric Current on the Reduction of Indigo Dye

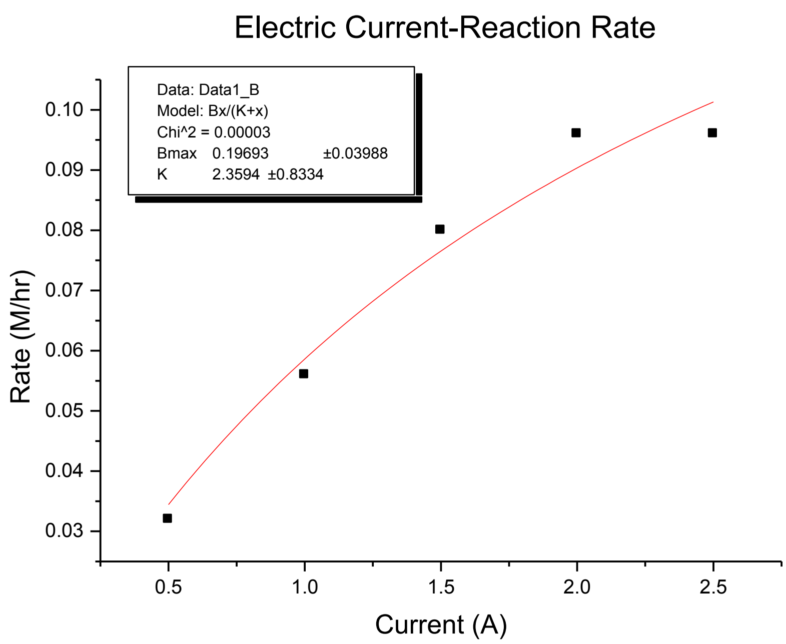


Figure 11. Electric current-Reaction rate.

These results suggest that when the electric current applied are high enough, a greater amount of hydrogen than used up is produced. When this happens, all reaction ports on the catalyst are occupied by reactants, and therefore the rate of the reaction depends solely on the ability of the catalyst to transfer active complexes into the final product, instead of the concentration of reactants. This leads to a maximum value of the reaction rate. This characteristic makes our reaction similar to the Michaelis Menton Model, for which the formula is

$$Rate = \frac{Rate\ \ max \times\ [S]}{[S] + K}$$

From this formula it was calculated that the maximum reaction rate is 0.197 M/hr.

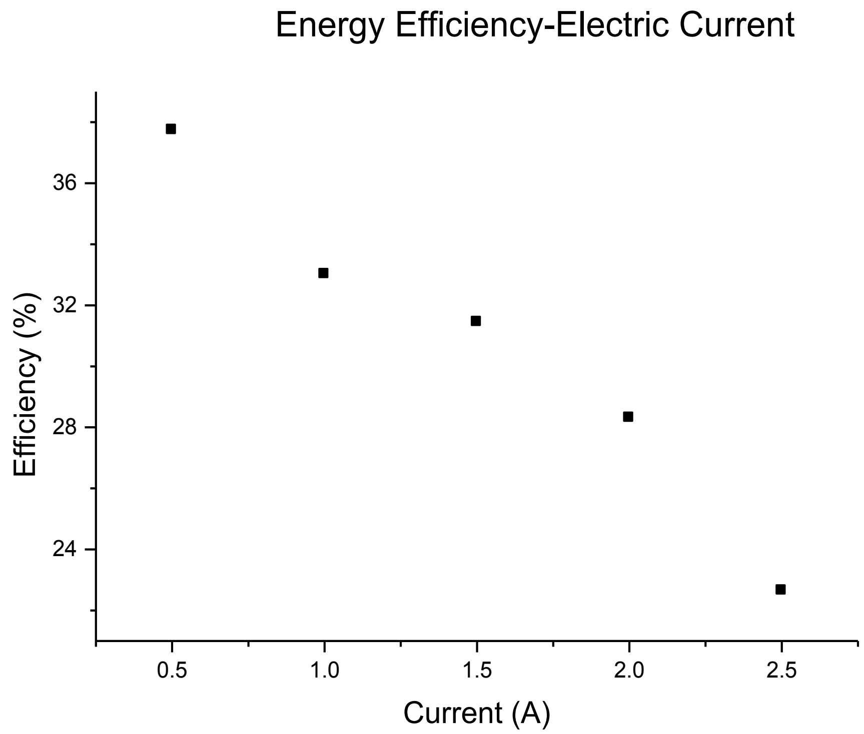


Figure 12. The Relationship between Energy Efficiency and Electric Current.

From Figure 12. it can be seen that the energy efficiency drops with the increase of electric current. From Fig.11, it is evident that when the electric current's amperage grows unlimitedly high, the efficiency of the reaction gradually approaches zero. Therefore the electric current is a vital means of controlling the speed and efficiency of the reaction. In industrial development of this technique, the electric current may be manipulated to reach the most desirable rate-efficiency ratio.

Also discovered through this experiment was that hydrogen left in the electrolysis tank after reaction could still catalyze the rest of the remaining Indigo Dye in the tank over 12 hours. Thus we extrapolated that if the shape of the catalyst or tank was modified to trap more hydrogen inside, the energy efficiency of the reaction could be greatly increased, saving more electricity, and therefore lowering the cost of the reaction.

4.3.4 Comparison of Efficiency of Electrolysis and the Traditional Method

The concentration of Indigo Dye on the pieces of gauze dyed in the two different ways was calculated to be 1.0×10^{-4} mole/1.052g gauze (traditional method) and 1.6×10^{-3} /1.052 g gauze (electrolysis method). The electrolysis method was able to, in the same time duration as the traditional method, cohere 16 times more Indigo Dye onto the same piece of cloth, which means it was16 times more efficient. This experiment thoroughly proves the excellence of electrolysis to the traditional method.

4.3.5 Comparing the Color Fade of Cloth dyed through the Traditional Method and the Electrolysis Method

The cloth dyed in the traditional way faded considerably after the first wash, whereas the cloth dyed through the electrolysis method showed little change even after being washed for 5 times. Figure 13. shows the marked difference in the color fade of the two cloths, clearly reflecting the excellence of the electrolysis method to the traditional method. (Appendix picture 4.)

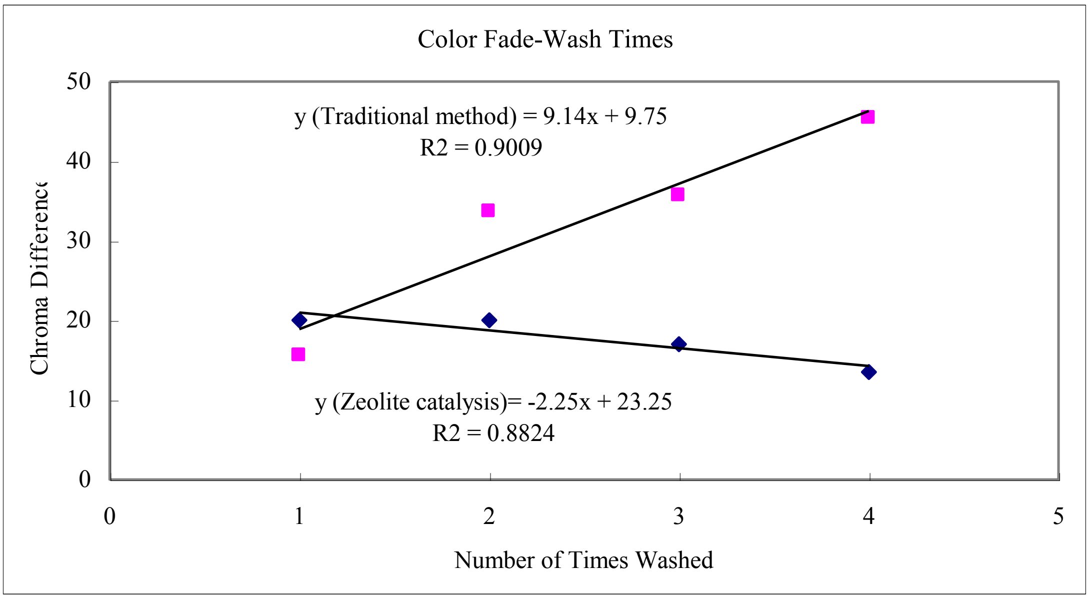


Figure 13. The relationship between color fade and wash rime.

In Figure 13. it can be seen that the chroma difference of the cloth dyed in the traditional way increased with time, meaning that the Indigo Dye washed off the cloth every time increased or at least did not lessen. Yet the chroma difference of the cloth dyed through Electrolysis decreased with time, meaning the Indigo Dye washed off greatly decreased every time. This means that Leuco Indigo coheres onto cloth much better than un-reduced Indigo Dye.

4.4 Disposal of Waste Indigo Dye

4.4.1 Preparation and Analysis of Fe-zeolite

Visibly, the Fe-Zeolite made through ion-exchanging was uneven in color, while Fe-Zeolite made through hydrothermal synthesis was very even. The catalysis rates of the zeolites accelerated with time.

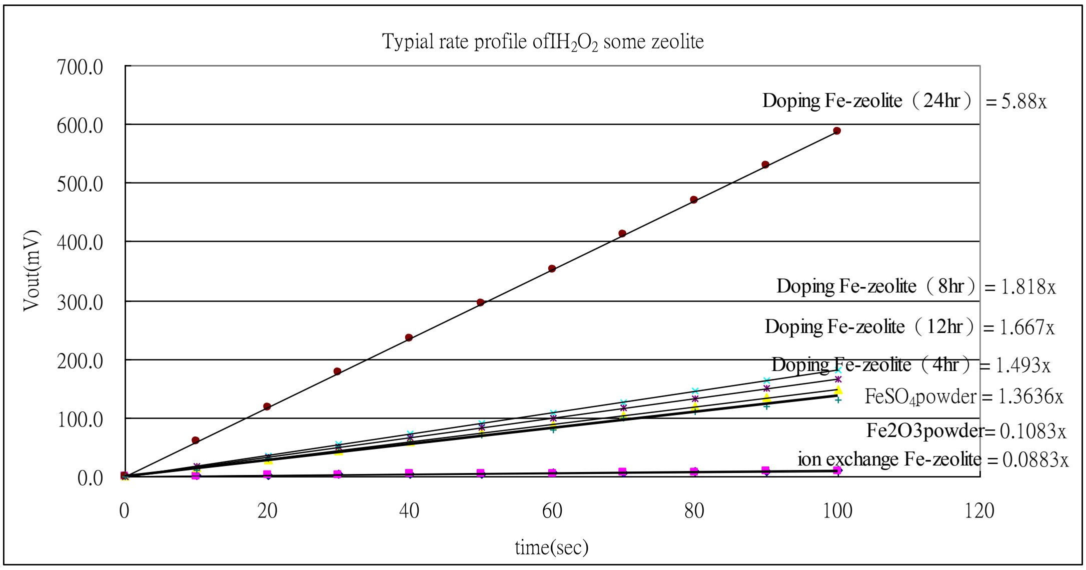


Figure 14. Reaction rate profile of H_2O_2 catalyzed by various zeolites.

The ion-exchange method was considered uneconomic, with even lower catalysis rates than Fe_2O_3. Although the $FeSO_4$ powder dissolved in the water, its reaction rate was still lower than that of the Fe-zeolite doped for 24 hours. It is known that Fe^{2+}

undergoes Fenton Reaction in the water, an homogeneous reaction, meaning high reaction rates. Yet Doping Fe-zeolite reacted even faster, suggesting that it may go through another reactive mechanism.

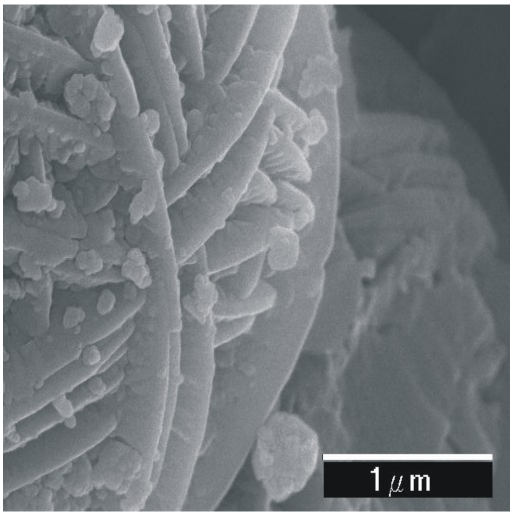


Figure 15. SEM image of the catalysts. (Fe-Al -SiO2)calcined at 623K for 2.5 hr.

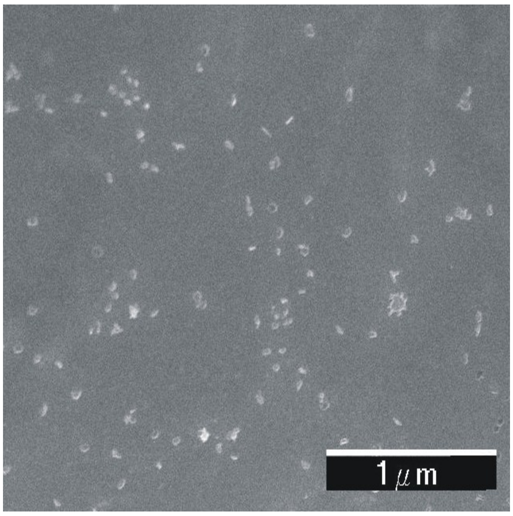
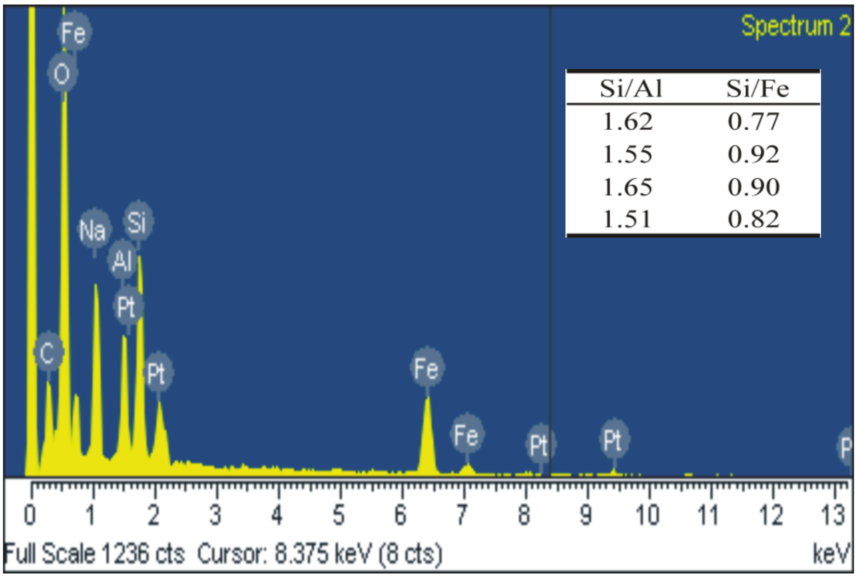


Figure 16. SEM image of the catalysts. (Fe-Al -SiO2)calcined at 873K for 2.5 hr.



Si/Al	Si/Fe
1.62	0.77
1.55	0.92
1.65	0.90
1.51	0.82

Figure 17. EDS analysis of the catalyst (Fe-Al-SiO_2).

The SEM image shows that the catalysts (Fe-Al-SiO_2) calcined at 623 K were rod-shaped with diameters of 150-200 nm. Calcined at higher temperatures (>873 K), the surface of the catalyst flattened, causing the catalyst to defunct. The molar ratios of Si/Al and Si/Fe determined by EDS suggest that iron is evenly dispersed in the catalyst calcined at 623 K.

4.4.2 Reaction Rate of Fe-zeolite-Electrode in Oxidizing Indigo Dye

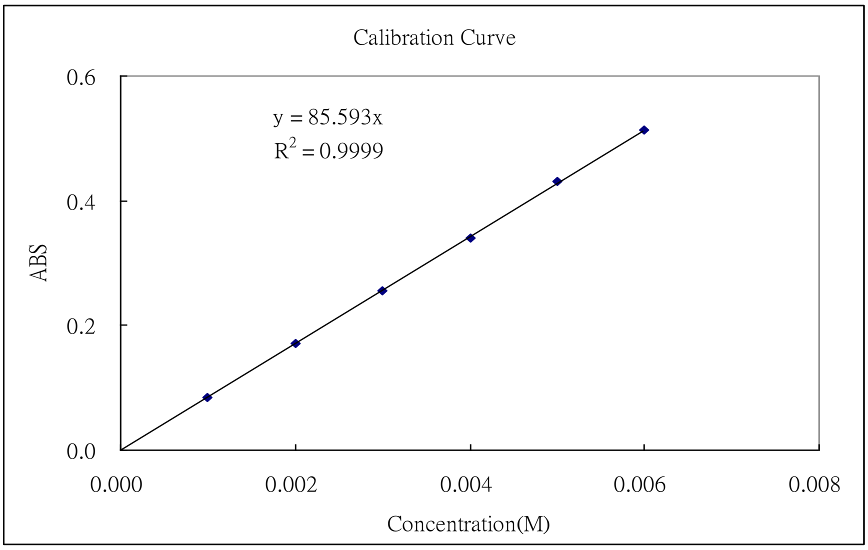


Figure 18. The calibration curve of ABS to Indigo dye concentration.

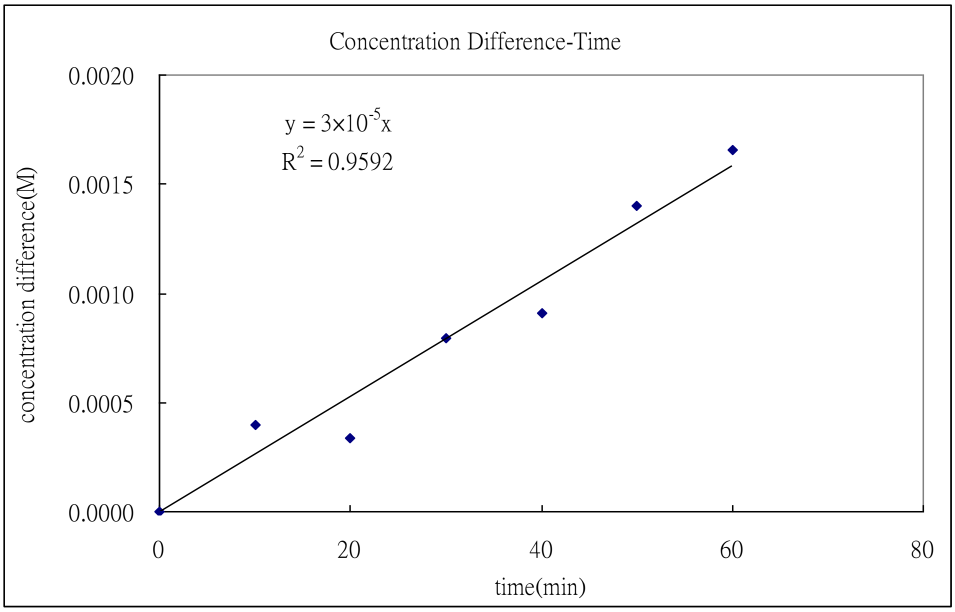


Figure 19. The rate of oxidization catalyzed by Fe-zeolites and electrolysis.

The concentration of waste Indigo Dye in the solution showed a significant drop under the catalysis of Fe-Zeolite. With a starting concentration of 0.006M, an electric current of 0.05A, and a 20 gram Fe-Zeolite Argil catalyst composed of 50% Fe-Zeolite and 50% Argil powder, the device was able to reach an average energy efficiency of 15.3%., and could oxidize 27.7% of the waste Indigo Dye in an hour.

5. Conclusions

This project improved many aspects of blue dyeing with natural Indigo Dye. Through the utilization of Zeolites and electrolysis, we successfully improved the reaction rate and energy efficiency as well as tackled the waste disposal problems of traditional blue dyeing while maintaining the use of all-natural Indigo Dye.

5.1 High Reaction Rate

The reaction rate of reduction of Indigo Dye was markedly increased through the use of Pt-Zeolites as catalysts. The traditional reduction process takes 1-3 weeks to complete, often depending on the weather condition. The electrolysis method takes only

2 hours to produce enough Leuco Indigo for dyeing. Moreover, depending on the size and shape of the catalyst argil, the electric current applied, and the concentration of Indigo Dye in the solution, the electrolysis method has been proved and can be expected to reach even higher rates. In the experiments performed, the highest recorded reaction rate was 0.096 M/hr. But to note is that this rate was achieved using a solution diluted from the Indigo paste used in traditional dyeing by $\frac{7}{500}\times\frac{5}{110}$ (ml). Thus it is believed that, since the Indigo Dye concentrations in our experiments were relatively low, there is much room for improvement of reaction rates through alternation of the concentration of Indigo Dye in the electrolysis solution.

5.2 High Energy Efficiency

There is no doubt that the electrolysis method excels the traditional method in terms of energy efficiency, a major concern for today's green industries. First of all, the electrolysis method utilizes easy-to-handle, easy-to-access electricity to create hydrogen for the reaction, whereas the traditional method uses biofermentation, a method that deploys micro-organisms to reduce Indigo Dye, and in which micro-organisms need to eat up energy to grow and reproduce, thus wasting energy and producing large amounts of carbon dioxide. Also, biofermentation requires a lot of care, and, worst yet, greatly contributes to air pollution, producing all kinds of terrible smelly waste gases in addition to carbon dioxide.

Second, electrolysis is performed in a closed system, in which there is no oxygen to oxidize the Leuco Indigo while the traditional method uses an open system, in which Leuco Indigo is being oxidized while Indigo Dye is being reduced. Therefore, more time and energy are needed for enough Leuco Indigo to be produced for dyeing. It is impossible to have the traditional method operate in a closed system since the micro-organisms required for biofermentation need oxygen to grow.

Third, the Indigo Dye that has gone through electrolysis can be used up repeatedly until it has been completely used up, while the Indigo Dye left over from the traditional process is over-decomposed and can only be disposed of, wasting considerable amounts of Indigo Dye. In the electrolysis process, not only can the Indigo Dye be repeatedly used for dyeing, when the Indigo Dye in the tank exhausts, more Indigo Dye added will keep the reaction going on. In all aspects, the electrolysis method was more energy-efficient than the traditional method.

5.3 Solutions to Waste Disposal

Because the traditional process of reducing Indigo Dye can only achieve very low reduction rates, the actual amount of Indigo Dye reduced into Leuco Indigo for dyeing was actually very small, which means that the coherent connections between the dye and the cloth was relatively weak because Indigo Dye does not dissolve in water and remain in the form of floating particles which are too big to attach onto the fiber of cloth, as depicted in Section 2.3.4. Conclusively this means that more Indigo Dye is washed off in the cleansing process, as demonstrated in Section 2.3.5, wasting more material and causing much more pollution than the electrolysis method, which has high reduction rates and produces almost no waste fluids at all. Also, less Indigo Dye cohered onto the cloth means more Indigo Dye in waste fluids, which would then require excessive treatment, such as particle settlement and colloid treatment, which causes even more pollution.

The common procedure nowadays of disposing of waste fluids is Fenton Reaction, which utilizes hydrogen peroxide and an iron catalyst to oxidize contaminants. Yet this reaction demands a highly acid environment (pH=2~4) and produces highly polluting ferric compounds. Furthermore, the reactants of the reaction become reduced with time, meaning that the reaction is harder to operate due to instable reactant percentages. In comparison, oxidizing Indigo Dye with Fe-Zeolite argil works in a slightly acid environment, produces no byproducts, and, when combined with the electrolysis apparatus, has great cost efficiency, and is extremely easy to operate.

Also, the two processes of reducing Indigo Dye and oxidizing waste fluids can be performed at the same time in the two sides of the electrolysis apparatus, making the electrolysis apparatus a double-functioning device, greatly simplifying operation, reducing cost, and, most important of all, when operating both functions at the same time, this raises the combined energy efficiency to more than 50%.

In conclusion, with our reaction taking a matter of hours while the traditional method taking weeks, our project not only successfully improved the reaction rate and energy efficiency, but also proposes a solution to the problems of air and water pollution of traditional blue dyeing. Through innovative designs and ideas, we have provided the traditional blue dyeing with a new potential in the current market of natural, eco-friendly commodity.

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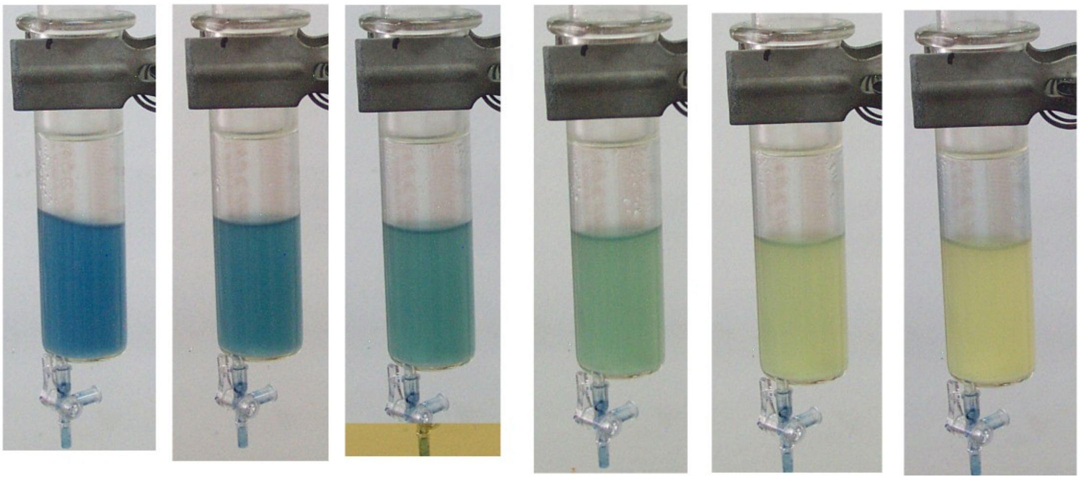
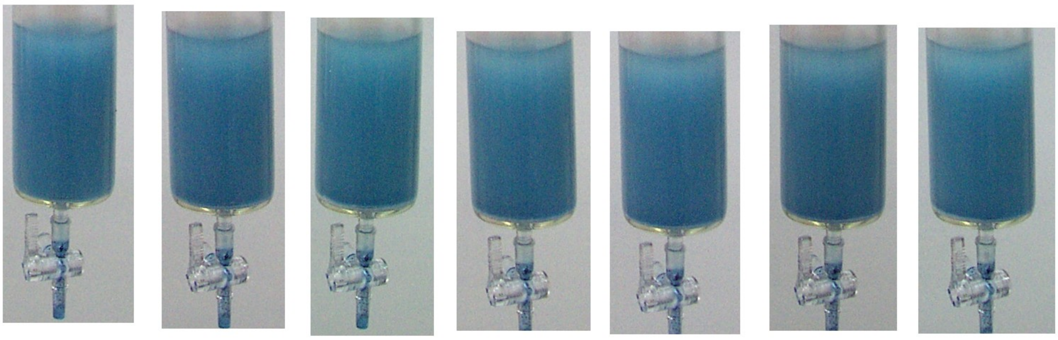
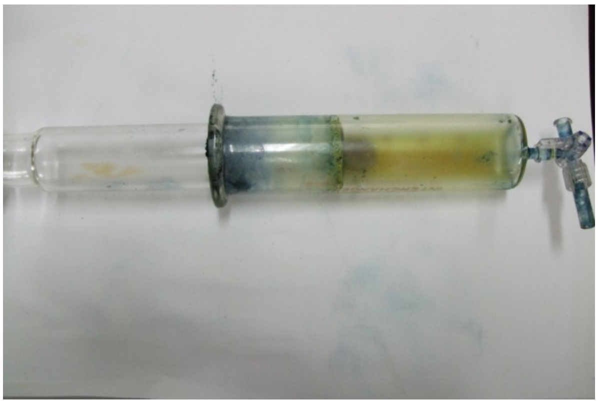
7. Appendix



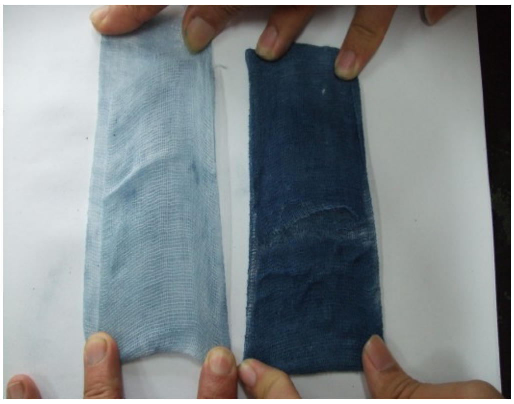
Picture 1　Low-Silicon Pt-zeolite Reaction Photos (from left, taken every 30 seconds).



picture 2.　Blank zeolite Reaction Photos (from left, taken every 30 seconds).

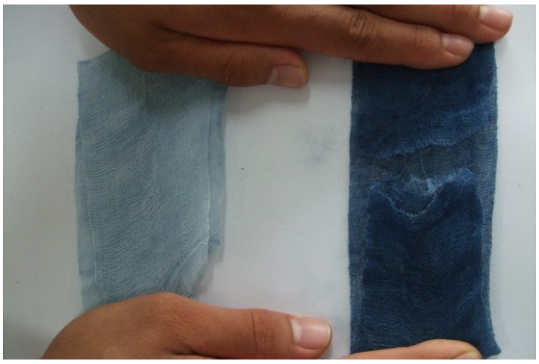


Picture 3.　Apparatus for the reduction of Indigo Dye using Pt-Zeolite Argil.



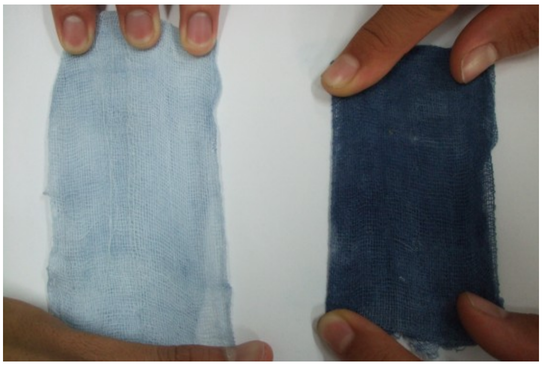
1st time

2nd time



3rd time

4th time



5th time

Picture 4. The comparison of the color fade of cloth dyed through the traditional method (left) and electrolysis (right).

評語

1.研究題目有不錯的創意，研究執行也有一定的深度及完整性。研究成果也具有可能的應用價值。

2.成果的展現可以更系統些，訴求之重點及主要成果也可表達的更明確。

3.產品穩定度之比較宜提供解釋及必要數據。