2022 年【全國科學探究競賽-這樣教我就懂】

高中（職）組 成果報告表單

題目名稱： Conditions For Building An Electrochemical Oxidation Model Pretreating Common Non-steroidal Anti-Inflammatory Drugs

一、摘要

A theoretical model is proposed to solve the ecological crisis of wastewater contamination from pharmaceutical drugs. We selected spectrophotometric analysis to help identify the concentration changes while manipulating independent variables that affect reduction magnitude. All data were analyzed using the F-Hypothesis ANOVA Tests and Tukey-Kramer posthoc. At the 95% confidence level, we found that temperatures below 25˚C and pH levels below 4 have the highest reduction. Inputting these factors into the proposed model, approximately 50% greater electrochemical oxidation ability was achieved in comparison with the control group. This model could be applied in rural or third-world countries without treatment plants, households with high drug usage, hospitals, and pharmaceutical factories.

我們透過分光光度法分析溶液的吸光度，以確定濃度變化；並在每個溶液內和所有組中分析溫度和 pH 值。我們採用變方分析(F-Hypothesis ANOVA)和事後比較檢定，以推導所有自變量的最大電化學氧化能力。研究結果表明，在 95% 的置信水平下，低於 25˚C 的溫度和低於 4 的 pH 值具有最高的還原能力。我們所提出的模型，使用最佳條件，呈現出大約 50% 的初始結果和比對照組更高的電化學氧化去除能力。這種模式可以應用於沒有處理廠的農村或第三世界國家、藥物使用率高的家庭以及醫院和製藥廠。

二、探究題目與動機

Recent news has shed light on the rampant ecological pollution in lakes, rivers, and estuaries in Taiwan, proliferating risk to local ecosystems and aquatic species. Curious and determined for a solution, we read related studies and realized that wastewater treatment plants’ poor removal efficiency of pharmaceutical wastes and subsequent improper disposal were major factors of pollution. After discussing our findings online, we concluded that past ecotoxicity studies synthesized that low concentrations of non-steroidal anti-inflammatory pharmaceutical drugs (NSAIDs) impose consequential toxicological threats. A common solution is an electrochemical oxidation, due to its environmental-friendly, precise, and flexible removal traits at large-scale wastewater treatment plants. However, no significant research was dedicated to finding the conditions for household pretreatment procedures, risking the exposed environment before wastewater reaches treatment plants. This study explores the optimal conditions to pretreat pharmaceutical wastewater conventionally in the household and proposes a theoretical model for electrochemical oxidation applicable as pretreatment.

三、探究目的與假設

<u>Experimental Goals:</u>

1. Identifying the optimal wavelength to detect sensitive changes in concentration levels after electrochemical oxidation through absorbance.
2. Measuring the effect of temperature and pH level on the effect of electrochemical oxidation when removing pharmaceutical compounds in solutions.
3. Comparing the optimal independent variables with the control variables, deriving a practical electrochemical oxidation model for pretreating pharmaceutical wastewater in the household.

Hypothesis: We predict these experimental solutions would be analyzed at low wavelengths, consistent with existing literature. Our hypothesis theorizes that increasing temperature levels and decreasing pH levels would increase the electrochemical oxidation magnitude of pharmaceutical components in combination and respectively.

四、探究方法與驗證步驟

Experimental Preparation:

- Procurement of Reagents: ethyl alcohol, citric acid monohydrate, acetylsalicylic acid, buffer solutions (pH 1 to pH 13), salicylic acid, acetaminophen.
- Preparation of Reagents: Per Wudarska et al. (2014), Chrześcijańska et al. (2013), and much other existing literature, two standardized levels of concentration were set for solid and liquid substances. The concentration of solid and liquid substances was prepared with a weight (g) to water (mL) ratio of 1:30 and 1:20 respectively.
- Electrochemical Cell: A two-electrode electrochemical cell with platinum anode and cathode (surface area of 5 mm^2) was employed. Solutions of approximately 50 mL were added into the beaker with supporting electrolyte of Na_2SO_4 and were purged to remove dissolved gases. The solutions were then electro-reduced by two 1.5-volt batteries, connected with alligator clips to the electrodes, for two minutes before being stirred and sampled for spectrophotometric analysis. Constant monitoring of experimental parameters through an ammeter and voltmeter were conducted to minimize error.
- Apparatus: beaker, pipette, digital balance, volumetric flask, watch glass, funnel, spatula, magnetic stirrer, platinum electrode, alligator wire, 1.5V battery, graduated cylinder, thermometer, pH meter, mortar, and pestle, wash bottle, magnetic plate heater and stirrer.
- Independent Variables: wavelength input (by intervals of 25 nm, temperature (by intervals of 5˚C), pH level (by intervals of 3 pH levels).
- Control Variables: STP conditions, electrode area of 5 mm^2, pH 7, and solution volume to electrode area ratio of 10:1.

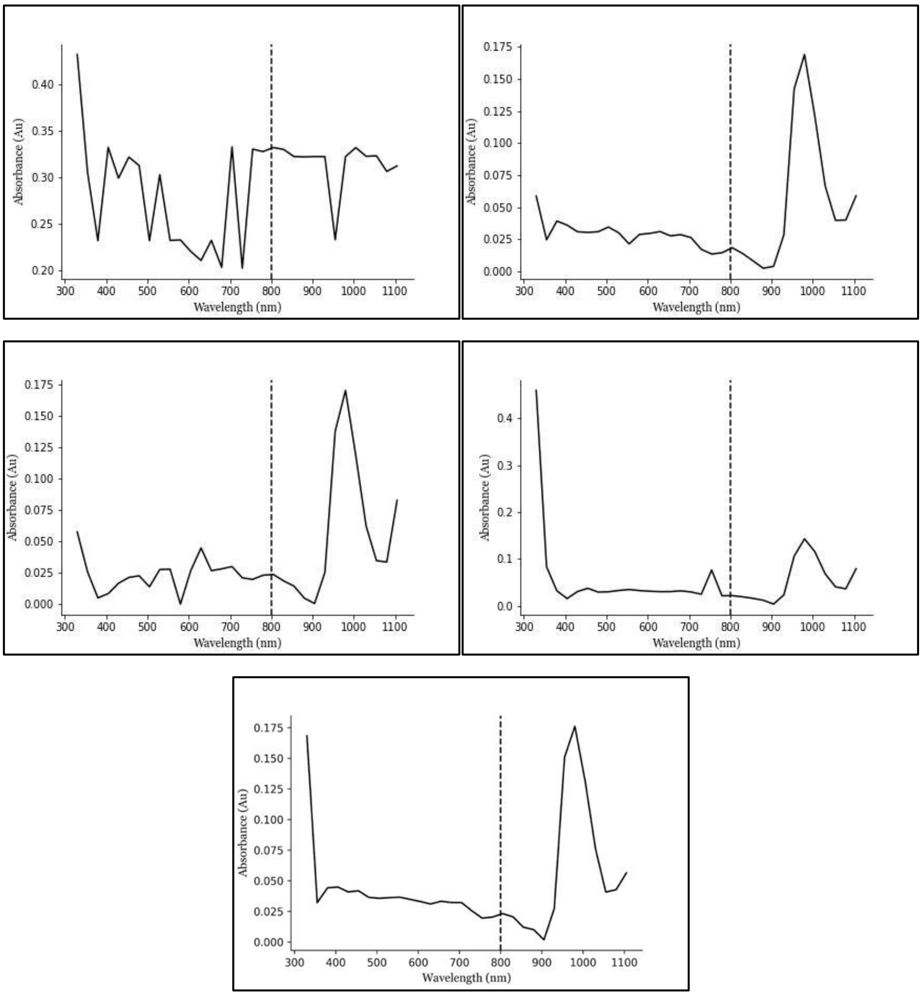
Methodology:

- Data Analysis: Statistical analysis was conducted using the SPSS Statistics Software and Python programming language in Jupyter Notebook. All data have passed Levene's Homogeneity of Variances before running the F Hypothesis ANOVA Test and the Tukey-Kramer posthoc test. Analyses were carried out at the 95% confidence level.
- Experimental Procedure: A pre-experiment was conducted to identify the optimal detection wavelengths. During the pre-experiment, solutions were scanned in 25 nm intervals from 330 nm to 1100 nm. Subsequent intervals were scanned if local maximum occurs under derivative tests between the 25 nm intervals. To ensure compliance with Beer Lambert's law, all wavelengths beyond the UV-VIS range were omitted. Experiment one sets temperature levels as the independent variable and tests by intervals of 5˚C from 5˚C to 50˚C. Experiment two analyzes the effects of pH levels at intervals of 3 pH from pH 1 to pH 13. The last experiment was conducted after analyzing the optimal results from previous experiments. The variables of electrode area to solution volume ratio of 1:10, 5˚C, and pH 4 were chosen to model a pretreatment device comparing with control group.
- Independent Variables: wavelength input (by intervals of 25 nm), temperature (by intervals of 5˚C), pH level (by intervals of 3 pH levels)

Pre-Experiment: Determining Optimal Wavelength for Analysis

Salicylic acid, acetylsalicylic acid, and citric acid monohydrate presented their maximum absorbance at approximately 980 nm in the near-IR range. These datasets are omitted due to a violation of Beer Lambert's Law. Follow-up procedures for the three sample solutions were conducted; it was found that the optimal wavelength surrounds 330 nm. Ethyl alcohol and acetaminophen consistently demonstrated an optimal wavelength at 330 nm throughout the experiment. Therefore, results in the pre-experiment direct the following experiments to analyze sample solutions at 330 nm, the lowest wavelength limit of the spectrophotometer.

Absorbance (Au) as a Function of Wavelength (nm) of All Sample Solutions

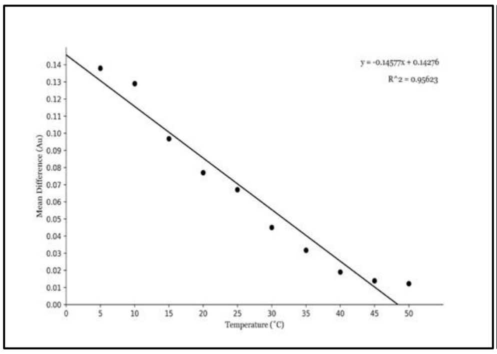


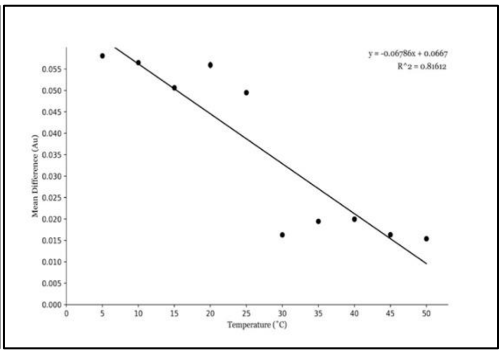
Note. Graphs of sample solutions are as follows: acetaminophen (top left), acetylsalicylic acid (top right), citric acid monohydrate (middle left), ethyl alcohol (middle right), and salicylic acid (bottom). A dashed line situated at 800 nm is used for identifying UV-VIS and IR spectrums.

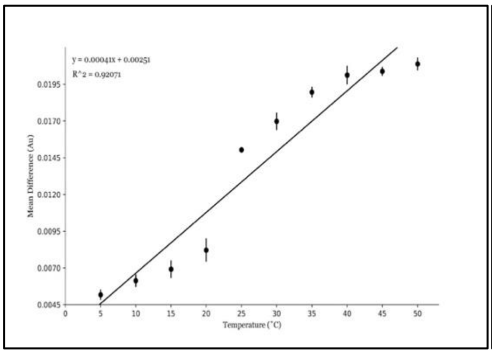
Experiment 1: Temperature

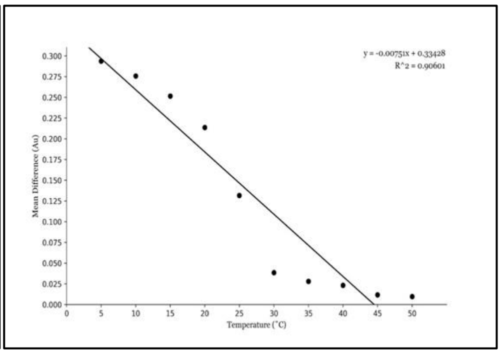
Salicylic acid, ethyl alcohol, and acetaminophen are electrochemically oxidized at higher temperatures whereas citric acid monohydrate demonstrated an inverse relationship (consistent linear regression slope of 0.00041 – the smallest in magnitude). After passing the F ANOVA test, it is evident that at the 95% confidence level all independent variables have different electroreduction means. Further analysis through the posthoc test derived three groups of homogeneous subsets: low temperatures (˚C < 25˚C), warm temperatures (25˚C < ˚C < 35˚C), and high temperatures (˚C > 25˚C). Overall, ethyl alcohol presented the strongest ability to electrochemically oxidize sample solutions below 40˚C whereas citric acid monohydrate has the weakest capacity.

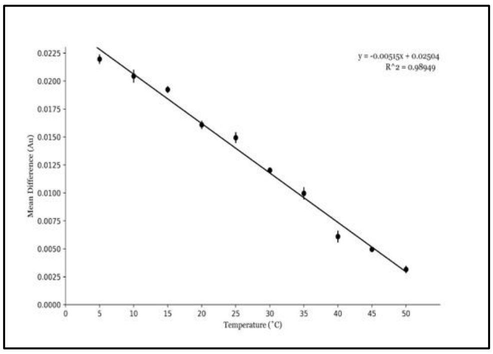
The magnitude of Mean Difference (Au) as a Function of Temperature (˚C) of All Sample Solutions









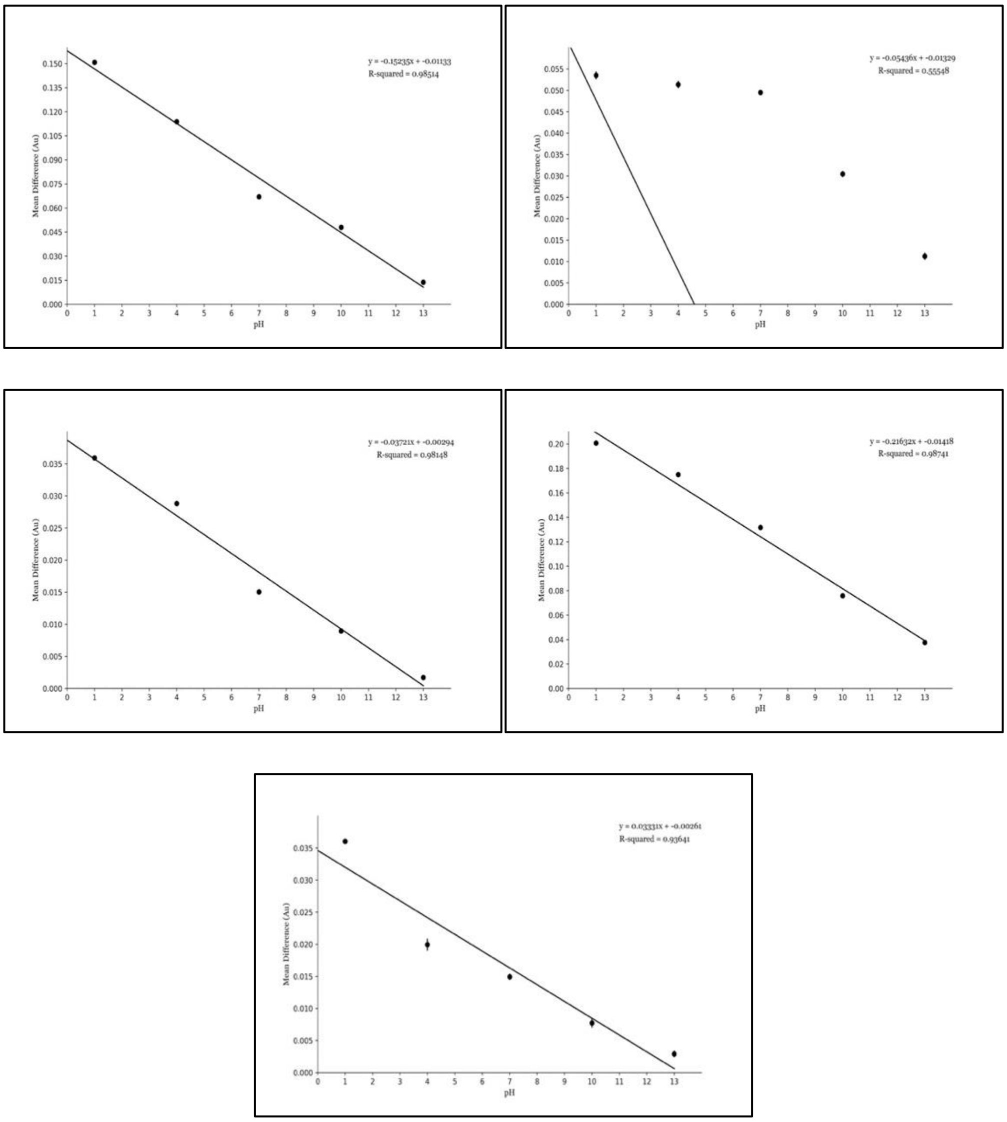


Note. Graphs of sample solutions are as follows: acetaminophen (top left), acetylsalicylic acid (top right), citric acid monohydrate (middle left), ethyl alcohol (middle right), and salicylic acid (bottom center)

<u>Experiment 2: pH Level</u>

There is a negative and linear proportional relationship between pH levels and the magnitude of electrochemical oxidation for all solutions. The R^2 value for acetylsalicylic is 0.555: the weakest linear relationship of all solutions. Citric acid monohydrate, on the other hand, presented the highest electrochemical oxidation ability followed by acetaminophen. After passing the F ANOVA test, it is evident that at the 95% confidence level all independent variables have different electroreduction means. Further analysis through the posthoc test derived four groups of homogeneous subsets: low pH levels (pH 1 < pH < pH 4), medium-low pH levels (pH 4 < pH < pH 7), medium-high pH levels (pH 7 < pH < pH 10), and high pH levels (pH 10 < pH < pH 13). The mean electroreduction magnitude of each homogeneous subset differs from one another by approximately 0.02 Au.

The magnitude of Mean Difference (Au) as a Function of pH of All Sample Solutions



Note. Graphs of sample solutions are as follows: acetaminophen (top left), acetylsalicylic acid (top right), citric acid monohydrate (middle left), ethyl alcohol (middle right), and salicylic acid (bottom center).

<u>Experiment 3: Overall</u>

F-hypothesis ANOVA test comparing the control with the prototype group with varying factors was carried out. We have 95% confidence that the prototype electroreduction device better removes pharmaceuticals overall compared with the control group. The approximate mean magnitude of electroreduction for the prototype is greater by 50% when compared to the control group.

SPSS ANOVA Result of Electroreduction Device vs Control Group for All Sample Solutions

	Sum of Squares	df	Mean Square	F	Significance
Between Groups	.038	1	.038	1335.35	<.001
Within Groups	.02	78	.000		
Total	.40	79			

Sum of Squares	df	Mean Square	F	Significance
.003	1	.003	184.661	<.001
.01	78	.000		
.004	79			

	Sum of Squares	df	Mean Square	F	Significance
Between	.004	1	.004	396.6	<.001

Sum of Squares	df	Mean Square	F	Significance
2.187	1	2.187	384	<.001

Groups				57	
Within Groups	.001	77	.000		
Total	.005	78			

				7.115	
	0.44	77	.001		
	2.231	78			

	Sum of Squares	df	Mean Square	F	Significance
Between Groups	.104	1	.104	11841.346	<.001
Within Groups	.001	77	.000		
Total	.105	78			

Note. Tables of sample solutions are as follows: acetaminophen (top left), acetylsalicylic acid (top right), citric acid monohydrate (middle left), ethyl alcohol (middle right), and salicylic acid (bottom center).

五、結論與生活應用

Overall, we conclude that the NSAIDs sampled in this research shall be analyzed under 330 nm due to spectrophotometer parameter limitations. Low wavelength setting is consistent with existing literature, which ranges from 250 nm to 350 nm. The results of experiment 1 ha refuted our hypothesis that higher temperatures facilitate electrochemical oxidation of pharmaceuticals. The results of experiment 2 – the lower the pH level the higher the electrochemical oxidation magnitude – are consistent with our hypothesis. When combining all the optimal factors (5˚C and pH 1), 50% greater active pharmaceutical compounds were electro-reduced.

<u>Real-Life Application</u>

Our proposed model to utilize electrochemical oxidation to pretreat pharmaceutical wastewater conventionally in the household allows various real-life applications. Such models could be implemented in rural or third-world countries, where few wastewater treatment plants are in proximity. Lack of funds and infrastructure made these areas prone to ecological pollution and environmental negligence. The model could slow this trend. In addition, this model could be installed in households where drug usage is frequent. Furthermore, it could be implemented near hospitals or pharmaceutical factories, where high drug production and consumption can create excess wastewater.

參考資料

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