UNIVERSITI PUTRA MALAYSIA

VOLTAMMETRIC DETERMINATION OF PALMITIC ACID BY ELECTRODE MODIFIED WITH REDUCED GRAPHENE OXIDE AND GOLD NANOPARTICLES COMPOSITE

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By

CHIN BOON CHING

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Chairman : Jaafar Bin Abdullah, PhD
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Palm oil is one of the most produced and traded vegetable oil in the world recently. The quality of palm oil is very important to be examined and one of the quality indices is free fatty acids (FFA) content. Palmitic acid is the major component of monosaturated acids in palm oil and hence is chosen in determination of FFA content. Acid-base titration method was traditionally used to determine acid content, but the presence of high amounts of carotene causes difficulties to determine the end point of the titration, causing inaccurate and inconsistent result. Development of alternative methods is needed to replace traditional method in order to remain competitive in world of industry. Thus, in this study, an electrochemical technique for the determination of FFA as alternative to conventional method (titration method) has been explored. The electrochemical method was developed based on electrochemically reduced graphene oxide (rGO) and reduced graphene oxide/gold nanoparticles (rGO/AuNPs) composite deposited onto screen-printed carbon electrode (SPCE) via drop-casting technique. The modified electrode was characterized by physico-chemical and electrochemical methods, respectively. Raman spectroscopy, Field Emission Scanning Electron Microscope (FESEM), Energy Dispersive X-Ray Spectroscopy (EDX) and Fourier Transform Infrared Spectroscopy (FTIR) all confirmed the successful formation of rGO and rGO/AuNPs. Redox signal of the modified electrode followed the order of rGO/AuNPs > rGO > AuNPs > bare > GO. The voltammetric behaviour of 2-methyl-1,4-naphthaquinone (VK_3) in the presence of palmitic acid at the modified electrode was investigated in an acetonitrile/water mixture containing lithium perchlorate ($LiClO_4$). The determination of palmitic acid was based on the voltammetric reduction of VK_3 to form corresponding hydroquinone which is proportional to the concentration of palmitic acid. Under optimum condition, the developed method showed a good linear relationship in the concentration ranging from

0.192 mM to 0.833 mM with the detection limit of 0.065 mM for rGO-modified SPCE and 0.040 mM for rGO/AuNPs-modified SPCE. For the validation study using t-test, the calculated t-values for both sensors were found to be less than the tabulated value which is 3.18, hence the difference between the two methods used is insignificant at the 95 % confident level and null hypothesis is accepted.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Master Sains

PENGESANAN ASID PALMITIK SECARA VOLTAMMETRIK BERDASARKAN ELEKTROD TERUBAHSUAI DENGAN KOMPOSIT GRAFIN OKSIDA TERTURUN DAN ZARAH NANO EMAS

Oleh

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Minyak kelapa sawit adalah salah satu minyak sayuran yang paling banyak dihasilkan dan diperdagangkan di dunia baru-baru ini. Kualiti minyak kelapa sawit amat penting untuk diperiksa dan salah satu indeks kualitinya adalah kandungan asid lemak bebas (FFA). Asid palmitik ialah komponen utama asid monotepu dalam minyak sawit, oleh itu dipilih dalam penentuan kandungan FFA. Kaedah pentitratan asid-bes telah digunakan secara tradisional dalam penentuan kandungan asid, namun kehadiran karotena yang tinggi menyebabkan kesukaran dalam menentukan titik akhir pentitratan, mengakibatkan keputusan yang tidak tepat dan tidak konsisten. Pembangunan kaedah alternatif adalah diperlukan untuk menggantikan kaedah tradisional bagi kekal kompetitif di dunia industri. Oleh itu, dalam kajian ini, teknik elektrokimia untuk menentukan kandungan FFA sebagai alternatif kepada kaedah konventional telah diterokai. Kaedah elektrokimia telah dibina berasaskan grafin oksida terturun secara electrokimia (rGO) dan komposit grafin oksida terturun/zarah nano emas (rGO/AuNPs) yang dilekatkan di atas elektrod karbon bercetak skrin (SPCE) melalui teknik sapuan titis. Elektrod yang telah diubahsuai telah dicirikan secara fiziko-kimia dan kaedah elektrokimia, masing-masing. Spektroskopi Raman, mikroskopi elektron pengimbas pancaran medan (FESEM), spektroskopi tenaga serakan sinar-X (EDX) dan spektroskopi inframerah transformasi fourier (FTIR) mengesahkan kejayaan dalam pembentukan rGO dan rGO/AuNPs. Isyarat redoks daripada elektrod yang diubahsuai mengikuti susunan rGO/AuNPs > rGO > AuNPs > elektrod pengosong > GO. Ciri voltammetrik 2-metil-1,4-naftakuinon (VK_3) dengan kehadiran asid palmitik pada elektrod yang diubahsuai telah dikaji di dalam campuran asetonitril/air mengandungi litium perklorat ($LiClO_4$). Penentuan asid palmitik adalah berdasarkan penurunan voltammetrik VK_3 untuk membentuk hidrokuinon sepadan yang berkadar dengan kepekatan asid palmitik. Pada keadaan optimum, kaedah

yang dibangunkan menunjukkan kelinearan baik pada julat kepekatan dari 0.192 mM sehingga 0.833 mM dengan had pengesanan 0.065 mM bagi SPCE yang diubahsuai dengan rGO dan 0.040 mM bagi SPCE yang diubahsuai dengan rGO/AuNPs. Bagi kajian pengesahan dengan menggunakan ujian t, nilai-t yang dikira bagi kedua-dua sensor adalah kurang dari nilai jadual iaitu 3.18, oleh itu perbezaan di antara dua kaedah adalah tidak signifikan pada tahap keyakinan 95% dan hipotesis nul diterima.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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Date: 10 June 2021

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LIST OF ABBREVIATIONS

Ag	Silver
AN	Acetonitrile
Au	Gold
AuNPs	Gold Nanoparticles
Cl	Chlorine
CdS	Cadmium Sulphide
COOH	Carboxyl Group
CPE	Constant Phase Element
CPO	Crude Palm Oil
CV	Cyclic Voltammetry
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
E°	Potential
e	Electron
ΔE_p	Peak-to-peak Separation Potential
EHEH	Electron Transfer/Proton Transfer/Electron Transfer/Proton Transfer
EIS	Electrochemical Impedance Spectroscopy
EDX	Energy Dispersive X-ray Spectroscopy
FESEM	Field Emission Scanning Electron Microscopy
$Fe(CN)_6^{3-/4-}$	Ferrocyanide Ion
FFA	Free Fatty Acids
FTIR	Fourier Transform Infrared Spectroscopy
GO	Graphene Oxide

GC	Gas Chromatography
GCE	Glassy Carbon Electrode
H^+	Hydrogen Ion
HPLC	High Performance Liquid Chromatography
I_D	Intensity of D Band
I_G	Intensity of G Band
I_p	Peak Current
K	Potassium
$K_3[Fe(CN)_6]$	Potassium Ferrocyanide
KCl	Potassium Chloride
KOH	Potassium Hydroxide
$LiClO_4$	Lithium Perchlorate
LOD	Limit of Detection
LSV	Linear Sweep Voltammetry
MPOB	Malaysia Palm Oil Board
Na	Sodium
$NaBH_4$	Sodium Borohydride
OH	Hydroxyl Group
P	Phosphorus
Pt	Platinum
Q	Quinone / Double-layer Capacitance
$Q^{\bullet-}$	Semiquinone
Q^{2-}	Quinone Dianion
QH_2	Hydroquinone
R&D	Research and Development

RBDO	Refined Bleached Deodorized Oil
R_{ct}	Charge-transfer Resistance
rGO	Reduced Graphene Oxide
RSD	Relative Standard Deviation
SD	Standard Deviation
SPCE	Screen-Printed Carbon Electrode
TiO_2	Titanium Oxide
TNTs	Titania Nanotubes
$V^{1/2}$	Square Root of Scan Rate
VK_3	Vitamin K_3 (2-methyl-1,4-naphthaquinone)

CHAPTER 1

INTRODUCTION

1.1 Palm Oil

The palm oil (Elaeis guineensis) is originally found from Western Equatorial Africa and leads to remarkable expansion of plantation throughout Southeast Asia. In the present-day world, one of the major oils and fats produced and commerce is palm oil which accounts for 30% of the world total in 2018 (Retrieved from https://ihsmarkit.com/products/fats-and-oils-industry-chemical-economics-handbook.html). Malaysia is the world's second-largest palm oil producer in 2018, contributing 19.52 million tonnes of crude palm oil (CPO) production (Din, 2019). In the past five decades, the increase of oil palm plantation side give rise to the production of crude palm oil due to Malaysia's climate, being hot and humid throughout the year and new innovation arising from R&D. Palm oil attracts much attention in industry because it is one of the cheapest oil in the market compared to other edible oils in the world such as soybean, rapeseed and sunflower oils, hence reduce the production cost (Azeman *et al*., 2015). Besides, palm oil use has grown significantly because of its edible properties and supply availability.

Palm oil has a balanced fatty acid composition in which the level of saturated fatty acids is almost equal to that of the unsaturated fatty acids. Palmitic acid (44%-45%) and monounsaturated oleic acid (39%-40%) are the major component acids, with polyunsaturated linoleic acid (10%-11%) and only a trace amount of linolenic acid. The others are largely stearic acid (5%) and myristic acid (1%). The minor constituents can be separated into two groups, namely fatty acid derivatives (partial glycerides (mono- and diacyl glycerols), phosphatides, esters and sterols) and non-glyceride constituents (sterols, triterpene alcohols, tocopherols, phospholipids, chlorophylls and carotenoids) (Ali and Abdurrhman, 2013). The palm oil can be extracted from two different parts of palm fruit which are either from the flesh of the fruit also known as mesocarp or from seed or kernel of the fruit. The mesocarp of the ripe palm fruits can give more amount of oil compared to the unripe one (Azeman *et al*., 2015).

The quality of palm oil is determined by many factors such as moisture, impurities, totox, odoriferous matter and iodine values but the most frequently determined quality indices is free fatty acids content during edible oils production, storage and marketing (Saad *et al*., 2007). The level of deterioration of oil has the direct influence towards the price of the palm oil in industry and it can be measured by free fatty acids content (Azeman *et al*., 2015). Fats and oils are esters of triglyceride and fatty acids. Hydrolysis can break down a fat or oil and subsequently release the glycerol and fatty acids, respectively by breaking the ester linkage. An enzyme called lipase catalyses the hydrolysis of the fats and oils. When the hydrolysis occurs the fatty acids will be released and thus lead to the undesirable saponification, low product yields, unpleasant smell and taste and difficulty in the subsequent separation processing steps (Azeman et al., 2015). Moreover, the physical damage of the palm fruits and prolonged storage of palm fruits may also lead to a significant increase in free fatty acids (FFA) content, thus affect the quality of palm oil. Standard determination for the FFA content (as palmitic acid) has been set by Malaysia Palm Oil Board (MPOB) which its composition in crude palm oil (CPO) and refined bleached deodorized oil (RBDO) should be less than 5 % and 0.1 %, respectively (Azeman *et al*., 2015).

1.2 Problem Statement

Food quality and safety are attracting more and more attention for producers, researchers, and consumers. Cooking oil is an essential food in daily life for home cooking and the food industry because of its unique biological and nutritional properties. The quality of such oils needs to be monitored as it will deteriorate slowly during storage and transportation process. In particular, one of the main quality parameters to reflect the quality of oil, degree of refining, as well as the quality change during storage is the FFA percentage which measures the extent of hydrolysis of triglycerides in edible oils (Rao *et al*., 2009). The lower the percentage of FFA in oil, the better the quality, fresh degree and degree of refining. High acidity degree of edible oil may lead to human gastrointestinal discomfort, diarrhoea and liver damage (Zhang *et al*., 2015).

The traditional way of determining free fatty acids in palm oil is through the acid-base titration method by titrating the sample against potassium hydroxide in hot 2-propanol solution, and phenolphthalein is used as an indicator (MPOB Test Methods, 2005). Theoretically, the acids present in the solution are neutralized during the titration and the volume of alkali used is proportional to free fatty acids content. Although this method is easy and straightforward, it is encountered with some problems such as time-consuming, labour-intensive and lack of accuracy (Jiang et al. 2016; Rao *et al*., 2009). In addition, during the neutralisation process, some samples contain coloured substances (mainly carotenoids which also known as pro-vitamin A) which causes difficulty to detect a subtle colour change of the indicator in the transition range, thus leads to the inaccurate result. Moreover, titration method is not sufficiently sensitive to detect a small acid concentration and a large amount of reagents and solvents are also consumed during the operation, thus resulting in increased costs and potential health and environmental hazards (Zhang *et al*., 2015).

Besides, many advanced methods are also utilised to measure the fatty acid content such as spectrophotometry, gas chromatography (GC) and high-performance liquid chromatography (HPLC). However, they involve tedious procedures as the extraction of palm oil prior to analysis, require skilled technicians to operate, time-consuming and involve high cost instrumentation (Fartas et al., 2017).

In order to stay in the competitive world of industry, alternative methods are clearly necessary to find out the needs to keep fulfilling the demands. The development of simple and accurate techniques to replace the old and traditional techniques for the detection of FFA amounts is a must. Therefore, electrochemical technique has attracted more and more attention nowadays by virtue of simple operation, rapid, sensitive, user-friendly and less expensive method for the detection of FFA. In electrochemical sensor development, much effort has been focused on developing nanomaterials with good electronic properties, stable, easily accessible by the analyte, and has a large surface area. Large surface area of the materials used plays the role in increasing the binding sites available for the detection of specific chemical analyte (Ma *et al*., 2013; Ahammad *et al*., 2009).

1.3 Objectives

The main objective of this research is to develop a simple and sensitive electrochemical sensor for an effective detection of palmitic acid in palm oil. Hence, two specific objectives have been identified to achieve the goal, including:

1. To prepare and characterize screen-printed carbon electrode (SPCE) modified with reduced graphene oxide (rGO) and nanocomposite reduced graphene oxide/gold nanoparticles (rGO/AuNPs).

2. To evaluate the analytical performance of the rGO and rGO/AuNPs-modified SPCE for the determination of palmitic acid content in palm oil using cyclic voltammetry (CV) and linear sweep voltammetry (LSV).

3. To validate the developed method with the standard method for the determination of palmitic acid content.

REFERENCES

Ahammad, A. J., Lee, J. J., & Rahman, M. (2009). Electrochemical sensors based on carbon nanotubes. *sensors*, *9*(4), 2289-2319.

Ali, A. S. M., & Abdurrhman, A. M. (2013). Determination of free fatty acids in palm oil samples by non-aqueous flow injection using salicyaldehyde-2, 4-dinitrophenylhydrazone as colorimetric reagent. *Chem. Mater. Eng*, *1*(3), 96-103.

Allen, J. B., & Larry, R. F. (2001). *Electrochemical methods fundamentals and applications*. John Wiley & Sons.

Amanulla, B., Palanisamy, S., Chen, S. M., Chiu, T. W., Velusamy, V., Hall, J. M., Chen, T., & Ramaraj, S. K. (2017). Selective colorimetric detection of nitrite in water using chitosan stabilized gold nanoparticles decorated reduced graphene oxide. *Scientific reports*, *7*(1), 1-9.

Astudillo, P. D., Valencia, D. P., González-Fuentes, M. A., Díaz-Sánchez, B. R., Frontana, C., & González, F. J. (2012). Electrochemical and chemical formation of a low-barrier proton transfer complex between the quinone dianion and hydroquinone. *Electrochimica acta*, *81*, 197-204.

Azeman, N. H., Yusof, N. A., & Othman, A. I. (2015). Detection of free fatty acid in crude palm oil. *Asian Journal of Chemistry*, *27*(5), 1569.

Azeman, N. H., Yusof, N. A., Abdullah, J., Yunus, R., Hamidon, M. N., & Hajian, R. (2015). Study on the spectrophotometric detection of free fatty acids in palm oil utilizing enzymatic reactions. *Molecules*, *20*(7), 12328-12340.

Bahadi, M. A., Japir, A., Salih, N., & Salimon, J. (2016). Free fatty acids separation from Malaysian high free fatty acid crude palm oil using molecular distillation. *Malaysian Journal of Analytical Sciences*, *20*(5), 1042-1051.

Benvidi, A., Dehghani-Firouzabadi, A., Mazloum-Ardakani, M., Mirjalili, B. B. F., & Zare, R. (2015). Electrochemical deposition of gold nanoparticles on reduced graphene oxide modified glassy carbon electrode for simultaneous determination of levodopa, uric acid and folic acid. *Journal of Electroanalytical Chemistry*, *736*, 22-29.

Cannan, S., Macklam, I. D., & Unwin, P. R. (2002). Three-dimensional imaging of proton gradients at microelectrode surfaces using confocal laser scanning microscopy. *Electrochemistry communications*, *4*(11), 886-892.

Chan, K. F., Lim, H. N., Shams, N., Jayabal, S., Pandikumar, A., & Huang, N. M. (2016). Fabrication of graphene/gold-modified screen-printed electrode for detection of carcinoembryonic antigen. *Materials Science and Engineering: C*, *58*, 666-674.

Da Silva, M. J., & Teixeira, M. G. (2017). An unexpected behavior of H 3 PMo 12 O 40 heteropolyacid catalyst on the biphasic hydrolysis of vegetable oils. *RSC Advances*, *7*(14), 8192-8199.

Din, A. K. (2019, January) Overview of the Malaysian Oil Palm Industry 2018. Retrieved from http://bepi.mpob.gov.my/images/overview/Overview _ of_Industry_2018.pdf

Elgrishi, N., Rountree, K. J., McCarthy, B. D., Rountree, E. S., Eisenhart, T. T., & Dempsey, J. L. (2018). A practical beginner's guide to cyclic voltammetry. *Journal of Chemical Education*, *95*(2), 197-206.

El-Hossary, F. M., Ghitas, A., Abd El-Rahman, A. M., Ebnalwaled, A. A., Fawey, M. H., & Shahat, M. A. (2020). Enhancement of Adhesion Force and Surface Conductivity of Graphene Oxide Films Using Different Solvents. *MS&E*, *762*(1), 012001.

Er, E., Çelikkan, H., Erk, N., & Aksu, M. L. (2015). A new generation electrochemical sensor based on Graphene nanosheets/Gold nanoparticles/Nafion nanocomposite for determination of Silodosin. *Electrochimica Acta*, *157*, 252-257.

Fartas, F. M., Abdullah, J., Yusof, N. A., Sulaiman, Y., & Saiman, M. I. (2017). Biosensor based on tyrosinase immobilized on graphene-decorated gold nanoparticle/chitosan for phenolic detection in aqueous. *Sensors*, *17*(5), 1132.

Fats and oils industry overview. Retrieved from https://ihsmarkit.com/products/fats-and-oils-industry-chemical-economics-handbook.html

Forster, R. J., Walsh, D., Adamson, K., & Spain, E. (2019). Voltammetry| Overview.

Gevaerd, A., Watanabe, E. Y., Fernandes, K., Papi, M. A. P., Banks, C. E., Bergamini, M. F., & Marcolino-Junior, L. H. (2020). Electrochemically Reduced Graphene Oxide as Screen-printed Electrode Modifier for Fenamiphos Determination. *Electroanalysis*.

Guin, P. S., Das, S., & Mandal, P. C. (2011). Electrochemical reduction of quinones in different media: a review. *International Journal of Electrochemistry*, *2011*.

Guo, W., Wu, L., Fan, K., Nie, D., He, W., Yang, J., Zhao, Z., & Han, Z. (2017). Reduced Graphene Oxide-Gold Nanoparticle Nanoframework as a highly selective separation material for aflatoxins. *Scientific reports*, *7*(1), 1-9.

Guy, O. J., & Walker, K. A. D. (2016). Graphene functionalization for biosensor applications. In *Silicon Carbide Biotechnology* (pp. 85-141). Elsevier.

Hayat, A., & Marty, J. L. (2014). Disposable screen printed electrochemical sensors: Tools for environmental monitoring. *Sensors*, *14*(6), 10432-10453.

Jampasa, S., Siangproh, W., Duangmal, K., & Chailapakul, O. (2016). Electrochemically reduced graphene oxide-modified screen-printed carbon electrodes for a simple and highly sensitive electrochemical detection of synthetic colorants in beverages. *Talanta*, *160*, 113-124.

Jian, J. M., Liu, Y. Y., Zhang, Y. L., Guo, X. S., & Cai, Q. (2013). Fast and sensitive detection of Pb2+ in foods using disposable screen-printed electrode modified by reduced graphene oxide. *Sensors*, *13*(10), 13063-13075.

Jiang, X., Li, S., Xiang, G., Li, Q., Fan, L., He, L., & Gu, K. (2016). Determination of the acid values of edible oils via FTIR spectroscopy based on the OH stretching band. *Food chemistry*, *212*, 585-589.

Khalil, I., Julkapli, N. M., Yehye, W. A., Basirun, W. J., & Bhargava, S. K. (2016). Graphene–gold nanoparticles hybrid—synthesis, functionalization, and application in a electrochemical and surface-enhanced raman scattering biosensor. *Materials*, *9*(6), 406.

Khoa, N. T., Kim, S. W., Yoo, D. H., Kim, E. J., & Hahn, S. H. (2014). Size-dependent work function and catalytic performance of gold nanoparticles decorated graphene oxide sheets. *Applied Catalysis A: General*, *469*, 159-164.

Kim, J., Chung, T. D., & Kim, H. (2001). Determination of biologically active acids based on the electrochemical reduction of quinone in acetonitrile + water mixed solvent. *Journal of Electroanalytical Chemistry*, *499*(1), 78-84.

Kim, R. S., Park, W., Hong, H., Chung, T. D., & Kim, S. (2014). Quinone electrochemistry altered by local hydrophobic environment and hydrogen bonding interactions. *Electrochemistry communications*, *41*, 39-43.

Kiroula, N., Negi, J. S., Singh, K., Rawat, R., & Singh, B. (2016). Preparation and characterization of ganciclovir-loaded glutathione modified gold nanoparticles. *Indian Journal of Pharmaceutical Sciences*, *78*(3), 313-319.

Kotani, A., & Kusu, F. (2002). HPLC with electrochemical detection for determining the distribution of free fatty acids in skin surface lipids from the human face and scalp. *Archives of dermatological research*, *294*(4), 172-177.

Kotani, A., Kusu, F., & Takamura, K. (2002). New electrochemical detection method in high-performance liquid chromatography for determining free fatty acids. *Analytica Chimica Acta*, *465*(1-2), 199-206.

Kumar, R., Kumar, A., Singh, R., Kashyap, R., Kumar, R., Kumar, D., & Kumar, M. (2020). Selective room temperature ammonia gas detection using 2-amino pyridine functionalized graphene oxide. *Materials Science in Semiconductor Processing*, *110*, 104920.

Lee, C. S., Yu, S. H., & Kim, T. H. (2018). One-step electrochemical fabrication of reduced graphene oxide/gold nanoparticles nanocomposite-modified electrode for simultaneous detection of dopamine, ascorbic acid, and uric acid. *Nanomaterials*, *8*(1), 17.

Li, J., Yang, J., Yang, Z., Li, Y., Yu, S., Xu, Q., & Hu, X. (2012). Graphene–Au nanoparticles nanocomposite film for selective electrochemical determination of dopamine. *Analytical Methods*, *4*(6), 1725-1728.

Liu, L., Li, Y., Liu, N., Li, X., & Wang, J. (2017). Differential Pulse Voltammetric Determination of Lactic Acid in Yogurts Based on Reduction of 1, 4-Benzoquinone. *Food Analytical Methods*, *10*(9), 3194-3200.

Lu, X., Wang, P., Wang, X., & Guo, Y. (2016). Electrodeposition of Gold Nanoparticles on Electrochemically Reduced Graphene Oxide for Sensitive Hydrazine Electrochemical Determination in Agriculture Wastewater. *Int. J. Electrochem. Sci*, *11*, 5279-5288.

Ma, X., Liu, Z., Qiu, C., Chen, T., & Ma, H. (2013). Simultaneous determination of hydroquinone and catechol based on glassy carbon electrode modified with gold-graphene nanocomposite. *Microchimica Acta*, *180*(5-6), 461-468.

MPOB (2005). MPOB Test Methods: A Compendium of Test on Palm Oil Products, Palm Kernel Products, Fatty Acids, Food Related Products and Others. Malaysian Palm Oil Board. Bangi.

Muhammad, N., Abdullah, J., Sulaiman, Y., & Ngee, L. H. (2017). Electrochemical Determination of 3-Nitrophenol with a Reduced Graphene Oxide Modified Screen Printed Carbon Electrode. *Sensor Letters*, *15*(2), 187-195.

Nanda, S., Gaur, A., & Duchaniya, R. K. (2020). Synthesis, properties and applications of graphene oxide: an overview. *World Scientific News*, *143*, 17-27.

Nazarpour, S., Hajian, R., & Sabzvari, M. H. (2020). A novel nanocomposite electrochemical sensor based on green synthesis of reduced graphene oxide/gold nanoparticles modified screen printed electrode for determination of tryptophan using response surface methodology approach. *Microchemical Journal*, *154*, 104634.

Parker, J. F., So, C. R., Sassin, M. B., Ko, J. S., Jeon, S., Chervin, C. N., Lytle, J. C., Helms, M. E., Rolison, D. R., & Long, J. W. (2020). Pyrolytic carbon films with tunable electronic structure and surface functionality: A planar stand-in for electroanalysis of energy-relevant reactions. *ChemElectroChem*, *7*(3), 672-683.

Pei, S., & Cheng, H. M. (2012). The reduction of graphene oxide. *Carbon*, *50*(9), 3210-3228.

Pocklanova, R., Rathi, A. K., Gawande, M. B., Datta, K. K. R., Ranc, V., Cepe, K., Petr, M., Varma, R. S., Kvitek, L., & Zboril, R. (2016). Gold nanoparticle-decorated graphene oxide: synthesis and application in oxidation reactions under benign conditions. *Journal of Molecular Catalysis A: Chemical*, *424*, 121-127.

Rao, Y., Xiang, B., Zhou, X., Wang, Z., Xie, S., & Xu, J. (2009). Quantitative and qualitative determination of acid value of peanut oil using near-infrared spectrometry. *Journal of food engineering*, *93*(2), 249-252.

Rashid, J. I. A., Yusof, N. A., Abdullah, J., Hashim, U., & Hajian, R. (2015). A novel disposable biosensor based on SiNWs/AuNPs modified-screen printed electrode for dengue virus DNA oligomer detection. *IEEE Sensors Journal*, *15*(8), 4420-4427.

Retrieved from http://www.dropsens.com/en/screen_printed_electrodes_pag.html

Retrieved from https://us.vwr.com/store/product/9881960/menadione-2-methyl-1-4-naphthoquinone-vitamin-k3-98

Retrieved from https://www.lunanano.com/product-page/gold-nanoparticles-citrate-coated

Saad, B., Ling, C. W., Jab, M. S., Lim, B. P., Ali, A. S. M., Wai, W. T., & Saleh, M. I. (2007). Determination of free fatty acids in palm oil samples using non-aqueous flow injection titrimetric method. *Food Chemistry*, *102*(4), 1407-1414.

Sadyraliev, D. (2018, March 16). Graphene Oxide – What Is It? Retrieved from https://nanografi.com/blog/graphene-oxide-what-is-it/

Shams, N., Lim, H. N., Hajian, R., Yusof, N. A., Abdullah, J., Sulaiman, Y., Ibrahim, I., Huang, N. M., & Pandikumar, A. (2016). A promising electrochemical sensor based on Au nanoparticles decorated reduced graphene oxide for selective detection of herbicide diuron in natural waters. *Journal of Applied Electrochemistry*, *46*(6), 655-666.

Shams, N., Lim, H. N., Hajian, R., Yusof, N. A., Abdullah, J., Sulaiman, Y., Ibrahim, I., & Huang, N. M. (2016). Electrochemical sensor based on gold nanoparticles/ethylenediamine-reduced graphene oxide for trace determination of fenitrothion in water. *RSC advances*, *6*(92), 89430-89439.

Song, M., Yu, L., & Wu, Y. (2012). Simple synthesis and enhanced performance of graphene oxide-gold composites. *Journal of Nanomaterials*, *2012*.

Sujiono, E. H., Zabrian, D., Dahlan, M. Y., Amin, B. D., & Agus, J. (2020). Graphene oxide based coconut shell waste: synthesis by modified Hummers method and characterization. *Heliyon*, *6*(8), e04568.

Takamura, K., & Hayakawa, Y. (1968). Polarographic determination of acids by means of the reduction wave of quinones in methyl cellosolve solution. *Analytica Chimica Acta*, *43*, 273-279.

Takamura, K., & Hayakawa, Y. (1971). Effects of proton donors on the polarographic reduction of methyl-p-benzoquinone in aqueous and methyl cellosolve solutions. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, *31*(1), 225-232.

Takamura, K., Fuse, T., Arai, K., & Kusu, F. (1999). A review of a new voltammetric method for determining acids. *Journal of Electroanalytical Chemistry*, *468*(1), 53-63.

Tang, Y., Huang, R., Liu, C., Yang, S., Lu, Z., & Luo, S. (2013). Electrochemical detection of 4-nitrophenol based on a glassy carbon electrode modified with a reduced graphene oxide/Au nanoparticle composite. *Analytical methods*, *5*(20), 5508-5514.

Toh, S. Y., Loh, K. S., Kamarudin, S. K., & Daud, W. R. W. (2016). The impact of electrochemical reduction potentials on the electrocatalytic activity of graphene oxide toward the oxygen reduction reaction in an alkaline medium. *Electrochimica Acta*, *199*, 194-203.

Uchida, Y., Kätelhön, E., & Compton, R. G. (2018). Linear sweep voltammetry with non-triangular waveforms at a microdisc electrode. *Journal of Electroanalytical Chemistry*, *823*, 465-473.

Wang, J., Wang, H., Guo, S., Jia, X., Zhong, Y., Han, Y., Lin, M., Wang, S., Zhao, F., Fu., J., & Zhao, J. (2014). The pH changes at the electrode surface caused the new voltammetric waves in PCET reactions. *Journal of The Electrochemical Society*, *161*(9), H443-H446.

Wang, J., Wang, T., Wang, S., Han, Y., Sun, Q., Zhong, Y., Zhao, J., Zhao, F., Wang, H., & Sun, L. (2014). An electrochemical approach for the direct measurement of buffer capacity. *Journal of The Electrochemical Society*, *161*(9), H555-H557.

Wang, N., Lin, M., Dai, H., & Ma, H. (2016). Functionalized gold nanoparticles/reduced graphene oxide nanocomposites for ultrasensitive electrochemical sensing of mercury ions based on thymine–mercury–thymine structure. *Biosensors and Bioelectronics*, *79*, 320-326.

Wang, X., & Zhang, X. (2013). Electrochemical co-reduction synthesis of graphene/nano-gold composites and its application to electrochemical glucose biosensor. *Electrochimica Acta*, *112*, 774-782.

Yang, J., & Gunasekaran, S. (2013). Electrochemically reduced graphene oxide sheets for use in high performance supercapacitors. *Carbon*, *51*, 36-44.

Yusof, N. H., Abdullah, J., Yusof, N. A., & Zainal, Z. (2018). Fabrication of Titania Nanotube and Its Application for Palmitic Acid Determination by Electrochemical Technique. *Sensor Letters*, *16*(10), 729-736.

Zhang, N., Qiu, H., Liu, Y., Wang, W., Li, Y., Wang, X., & Gao, J. (2011). Fabrication of gold nanoparticle/graphene oxide nanocomposites and their excellent catalytic performance. *Journal of Materials Chemistry*, *21*(30), 11080-11083.

Zhang, W., Li, N., Feng, Y., Su, S., Li, T., & Liang, B. (2015). A unique quantitative method of acid value of edible oils and studying the impact of heating on edible oils by UV–Vis spectrometry. *Food chemistry*, *185*, 326-332.

Zhang, Z., Chen, H., Xing, C., Guo, M., Xu, F., Wang, X., Gruber, H. J., Zhang, B., & Tang, J. (2011). Sodium citrate: a universal reducing agent for reduction/decoration of graphene oxide with au nanoparticles. *Nano Research*, *4*(6), 599-611.

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