# UNIVERSITI TEKNOLOGI MARA

# SYNTHESIS, CHARACTERISATION AND CORROSION INHIBITION MECHANISMS ON MELDRUM'S ACID DERIVATIVES: EXPERIMENTAL AND THEORETICAL STUDIES

**NUR AIMAN NAJWA BINTI KAMARUL BAHARIN**

Thesis submitted in fulfilment
of the requirements for the degree of
**Master of Science**
**(Chemistry)**

**Faculty of Applied Sciences**

**October 2025**

# ABSTRACT

Four derivatives of Meldrum's acid in this study were successfully synthesised: Vanillin Meldrum's acid (VanMA), 4-nitrobenzaldehyde Meldrum's acid (NitroMA), Benzaldehyde Meldrum's acid (BenMA) and 4-formylbenzonitrile (FormylMA). In ATR-FTIR analysis, a distinct stretching band corresponding to ν(C=O) was detected between 1698 – 1790 $cm^{-1}$, confirming the presence of the Meldrum's acid. Specific functional groups are identified for each compound in which VanMA, showed OH peaks (3337 $cm^{-1}$), NitroMA exhibited *p*-$NO_2$ peak (852 $cm^{-1}$) and FormylMA displayed a C≡N peak (2238 $cm^{-1}$). $^{13}C$ NMR identifies a peak between 162-164 ppm, corresponding to C=O. Single crystal X-ray crystallography confirmed the structure of VanMA and BenMA, with VanMA crystallizing in the triclinic system with *P*-1 space group and BenMA crystallizing in the monoclinic system with $P12_11$ space group, which these space group define the arrangement of the atom in solid. The corrosion inhibition potential of these compounds in 1M hydrochloric acid (HCl) on mild steel was evaluated through weight loss (WL) analysis, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarisation (PDP) and surface analysis. FormylMA demonstrated the highest inhibition efficiency, achieving 94.86% (WL), 94.11% (EIS) and 77.89% (PDP) at a concentration 0.1mM. PDP results indicated that all inhibitors acted as mixed-type inhibitors, predominantly suppressing the cathodic reaction. Scanning electron microscopy (SEM) revealed a smoother surface in the presence of inhibitors compared to the blank sample. Energy dispersive x-ray (EDX) mapping confirmed the adsorption of inhibitors, evidenced by the presence of oxygen and nitrogen elements on the mild steel. Atomic force microscopy (AFM) further supported this observation, with the FormylMA-treated surface exhibiting reduced roughness (102 nm) compared to the blank sample (356 nm). X-ray photoelectron spectroscopy (XPS) confirms Fe-O and C=O peaks, indicating interaction via oxygen in chemisorption. Adsorption studies suggested that all Meldrum's acid derivatives followed the Langmuir isotherm, suggesting the formation of a monolayer of inhibitor molecules on mild steel. Gibbs free energy calculation suggested chemisorption for all inhibitors, while PDP showed mixed adsorption. WL analysis shows that VanMA and NitroMA preferred mixed adsorption while BenMA and FormylMA favoured chemisorption. Molecular Electrostatic Potential (MEP) analysis highlighted high electron density around the carbonyl oxygen in Meldrum's acid, $NO_2$ oxygen in NitroMA and CN nitrogen in FormylMA, suggesting these atoms are the primary sites for electron donation to mild steel. Mulliken analysis confirmed oxygen, nitrogen and aromatic ring as key adsorption sites. In 1M HCl, the substituents influenced protonation sites, with VanMA favour OH deprotonation, NitroMA and FormylMA favoured nitrogen protonation, and BenMA preferred carbonyl oxygen protonation which leads to physisorption. Meldrum's' acid derivatives have the potential to inhibit corrosion by adsorbing onto the mild steel with oxygen atoms adsorbing via chemisorption, protonated oxygen and nitrogen, and deprotonated oxygen via physisorption in acidic conditions. Overall, experimental analysis supported by DFT study confirmed that the corrosion inhibition mechanism of Meldrum's acid derivatives involves mixed adsorption where both electrostatic physisorption and chemisorption, contribute to the formation of protective layer on mild steel surface.

# ACKNOWLEDGEMENT

In the name of Allah, the most Gracious, the Most Merciful,

As I reach the conclusion of this academic journey, I am filled with an overwhelming sense of gratitude for those who have stood by me with steadfast support and encouragement every step of the way. Above all, I owe my deepest thanks to my parents. To my mother, whose love, prayers and unyielding strength have been a guiding light throughout my life and to my father, Kamarul Baharin Mansor, whose wisdom and teaching continues to resonate within my heart. To my siblings, Muhammad Alif Aiman, Muhammad Adeeb Aiman and Muhammad Aqib Aiman, your love, patience and unwavering support have been an invaluable source of strength during this journey.

I am profoundly grateful to my esteemed supervisors, Assoc. Prof. Dr. Nur Nadia Dzulkifli, Assoc. Prof. Dr. Sheikh Ahmad Izaddin Sheikh Mohd Ghazali, and Dr. Noorhidayah Pungot. Your scholarly guidance, encouragement and belief in my potential have propelled me forward and played a pivotal role in my academic success. May Allah reward you richly for your dedication and mentorship.

I am equally indebted to Dr. Monica Ahmad, Dr. Kavirajaa Pandian Sambasevam and my seniors, whose expertise and guidance in the realm of Electrochemical studies have been indispensable. May Allah bless you all for your dedication to nurturing knowledge.

To my dear friends, Syafarina, Alia, Syahirah, Adrina, Muiz, Syafiqah and Azhan, your friendship, encouragement and shared experiences have been constant source of joy and resilience throughout this journey. I also extend my deepest gratitude to all my friends during my Master's journey who have walked this path with me through both struggles and triumphs.

Lastly, I ask Allah, the Most Compassionate, to accept this work as a humble offering of knowledge. May He bless all those who have supported me throughout this journey, and may this work be a means to seek His pleasure, benefiting the broader community.

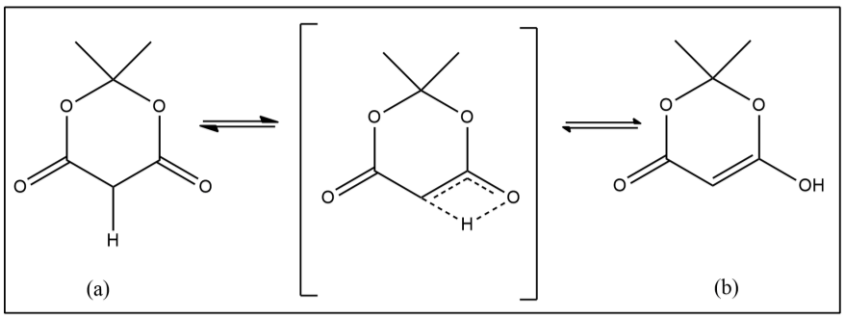
# TABLE OF CONTENTS

# CHAPTER 1
# INTRODUCTION

## 1.1 Research Background

### 1.1.1 Meldrum's Acid

Isopropylidene malonate (2,2-dimethyl-1,3-dioxane-4,6-dione), often known as Meldrum's acid, is a cyclic ester which is widely used as nucleophile in reactions for the synthesis of organic compounds (Filho et al. 2020). The six-membered ring's rigid structure and the CH2 moiety located between the two electron-withdrawing carbonyl (C=O) groups give Meldrum's acid an outstanding C-H acidity (Adnan et al., 2021). This high acidity allows it to easily form enolate ion, which act as nucleophile in the Knoevenagel condensation. In polar solvent like ROH (R = alkyl group) and DMSO, the enolate ion can exist in enol (b) tautomer, as shown in Scheme 1.1.




Scheme 1.1 Tautomerism of Meldrum's acid

In this process, Meldrum's acid combines with aldehyde (vanillin, 4-nitrobenzaldehyde, benzaldehyde, and 4-formylbenzonitrile) through Knoevenagel condensation to form highly activated arylidene Meldrum's acid derivatives as shown in Scheme 1.2. These derivatives are excellent Michael acceptor, which then can further undergo a Michael addition in one-pot synthesis (Filho et al., 2020). Numerous biological benefits are exhibited by its derivatives, including antioxidant activity, antibacterial, antituberculosis, and antimalarial properties Meldrum's acid also can be beneficial in preventing corrosion because of its ability to form protective layer, which