LAPORAN AKHIR

GERAN PENYELIDIKAN FRGS 203/PKIMIA/670031

ELUCIDATION OF STRUCTURE/ACTIVITY RELATIONSHIP AND INHIBITION MECHANISM OF TANNIN MONOMERS FROM COMPUTATIONAL CHEMISTRY PERSPECTIVES

ARPIL 2005

PREPARED BY

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FINAL REPORT

A. **PROJECT DESCRIPTION** **Date of this report: 12 April, 2004**

1. **Account No:** 2 0 3 6 7 0 0 3 1

2. **Project Title:** **Elucidation of Structure of Structure/Activity Relationship and Inhibition Mechanism of Lanthanides Salts from Computational Perspectives**

3. **Project Leader:** **Dr. Rohana Adnan**

4. **Co-researchers:** **Puan Afidah Abd. Rahim**

5. **This report is from** **Jan** *(month)* **to April 2005** *(month)*

6. **Starting date of project:** **November 2002** *(month)*

6. **What was the duration of the project?** 2 4 months

7. **This project was completed:** a ☐ within the period originally proposed; or
b ☑ extended beyond the proposed period

8. **a. Original project objectives** *[As described in the application form]*

The aims of the project are as follows: (i) to study the adsorption behavior of a wide range of lanthanide compounds (LX_3 where L = Ce, Ln, Y, and X= Cl, NO_3, SO_4) as corrosion inhibitors on Aluminium surface using computational approaches; (ii) to characterise chemically and physically the protective films of corrosion inhibitors using molecular modeling calculations; (iii) to develop a structure/activity relationship for the corrosion inhibitors

b. Objectives achieved *[State the extent to which the project objectives were achieved]*

Due to the computational power limitation, we have changed the study to tannins monomer, that is catechin, epi catechin while maintaining the overall original objectives.

c. Objectives not achieved *[State the objectives that were not achieved and explain why]*

Specifically, the original proposal aims at studying Lanthanides salts as an alternative to the present corrosion inhibitor

9. **What were the total project expenses?** RM_ 64,300_____

10. **Abstract of main findings:** *[Please describe in not more than 200 words in Bahasa Malaysia and English major/critical findings of the project. This abstract is for publication in USM's Annual Research Report. For additional space, please attach].*

Suatu kajian permodelan molekul telah dijalankan ke atas katecin, suatu flavanoid tanin dengan formula molekul $C_{15}H_{12}O_5OHH$ dan Fe^{3+} membentuk kompleks ferik tanat, Kaedah yang digunakan adalah semi empirikal, AM1 dan kaedah B3PW91/6-31G** dari teori fungsi densiti (DFT), yang masing-masing terdapat dalam perisian CAChe version 5.0 dan Gaussian 03. Pengoptimuman geometri dijalankan ke atas kedudukan kumpulan OH pada gelang A, C dan B menggunakan sudut dihedral permulaan, FeOCC = -90°, +90° dan 180°. Keputusan pengiraan tenaga yang konsisten diperoleh dengan menggunakan kedua-dua kaedah ini. Hasil kajian menunjukkan kedudukan Fe^{3+} pada gelang C memberikan tenaga paling rendah keseluruhan. Kajian ini bagaimanapun menunjukkan pengkompleksan pada gelang C adalah paling tidak mungkin berlaku berikutan ikatan hidrogen daripada kumpulan OH (katecin) terputus dan seterusnya membentuk ikatan dengan Fe^{3+}. Pengkompleksan katecin ke atas Fe^{3+} pada kedudukan di antara dua kumpulan hidroksil, pada gelang B pula memberikan tenaga keseluruhan dan permukaan tenaga potensi paling rendah berikutnya iaitu -4426.035 eV dan -2293.377 a.u masing-masing. Jarak Fe···O pada kedudukan ini, iaitu 1.96 Å, juga adalah konsisten dengan nilai eksperimen berbanding pada kedudukan gelang C yang 20 kali lebih panjang. Perbandingan tenaga orbital $E_{HOMO-LUMO}$ terhadap kesemua konformasi ferik-tanat, bagaimanapun menunjukkan kompleks Fe^{3+}-katecin pada kedudukan antara 2 kumpulan hidroksil gelang B merupakan suatu kompleks yang reaktif dan tidak stabil. Kesimpulannya, kajian ini menunjukkan kemungkinan katecin bertindak sebagai agen penukar karat iaitu dari karat aktif kepada karat tidak aktif.

Kata kunci: Katecin, penukar karat, ferik-tanat, semi empirikal, B3PW91/6-31G**

ABSRACT

A molecular modeling study of catechin, a flavanoid of tanin, with a molecular formula of $C_{15}H_{12}O_5OHH$ with Fe^{3+}, to form ferric-tannate complex, was performed using semi empirical AM1 method available on CAChe version 5.0 and density functional theory (DFT), B3PW91/6-31G** on Gaussian 03 programmes. Geometry optimization was performed based on the OH binding sites for all A, B and C rings of the catechin, using initial FeOCC dihedral angles of -90°, +90° and 180°. No geometrical constraints was applied throughout. Both methods consistently produced the overall energy trend. Result also shows binding at the C ring has the lowest overall total energy. However, complexation at this binding site is not likely to occur following an OH bond breaking, i.e. to form Fe-H bond instead. The next lowest energy conformation corresponds to the binding of Fe^{3+} to the B ring between the two OH groups. The average Fe-O distance, 1.96 Å, is also consistent with the experimental value compared to the binding at C ring which is 20 times longer. $\Delta E_{HOMO-LUMO}$ results also support the finding above, but further indicate that the Fe^{3+} binding at B ring, however is reactive and not stable. Therefore, it is concluded that catechin could probably reacts as a rust converter agent, that is to turn the active rust into its passive form.

Keywords: Catechin, rust converter, ferric-tannate, semi empirical, B3PW91/6-31G**

11. **Please provide a maximum of 5 key words which describe your research project (these key words will be keyed into the university's research database).**

Molecular Modeling, tannin, catechin, ferric tannate, rust converter

B. RESULTS AND OUTPUTS

12. **To the best of your knowledge, to which *core research activities* (i.e. *niche* research areas) at USM that your project may have contributed and/or strengthened? Please explain briefly.**

Surface Science and Corrosion

13. **This project has** [*please ✓appropriate box]*

	ITEMS	YES	NO
a	resulted in human resource training	√	
b	been patented		√
c	trained post-graduate students	√	
d	received other sources of funding		√
e	activated communication with other researchers, both local and international	√	
f	others (please specify)		

For each box ✓, please give details *[such as source, amount, type/nature, masters or PhD, name of agency and/or students, countries, etc.].*

1. **One Undergraduate training through final year project studies**
2. **Training of one (1) PhD student**

C. BENEFITS OF THE PROJECT

14. **Outputs of the Project and Potential Beneficiaries** *[Please describe as specifically as possible the outputs achieved and provide an assessment of their potential and their significance to the advancement of knowledge in the relevant areas].*

__USM as the center of Excellence in the field of Corrosion Science and also Computational Molecular Modelling

15. **Organisational Outcomes** *[Please describe as specifically as possible the organisational benefits arising from the project and provide an assessment of their significance].*

Collaborations between researchers in the PPS Kimia and also with International researchers, Universite Henri Poincare, Nancy, France

16. **National Impact** *[Please describe as specifically as possible the organisational benefits arising from the project and provide an assessment of their significance].*

D REPORTS, PAPERS AND PUBLICATIONS

17. List of reports and conference/seminar papers written:

18. List of scientific publications *[including name(s) of co-author(s), date of publication, location and name of publisher. Please attach pre-print or re-print copies of the publications]*

1. Paper submitted to the International Conference, EUROCORR 2004, in Nice (as attached) & presented in Sept. 2004

2. Paper submitted to Journal of Corrosion Science, Submitted March 2005 as attached.

3. One final year project student thesis

E. EQUIPMENT PURCHASED

19. **Please list out the equipment purchased for the project**

No	ITEMS	Price	Date of Purchase
1	2 Workstation	7,000	Jan 2003
2			
3			
4			
5			

F. OTHER INFORMATION

20. **Please provide other relevant information which you think would be useful to future research activities at USM, especially those that are related to the project which you have completed.**

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21. **Please provide reprint(s), galley proof(s), paper(s), or chapter(s) which should reflect the final results and findings of the research. All publications must acknowledge the grantee. A copy of all published article(s) or chapter(s) must be sent to the R&D Office.**

SIGNATURE : _____