DEVELOPMENT AND OPTIMIZATION OF ORGANIC-BASED CHEMOSENSOR FOR CATION AND ANION RECOGNITION IN AQUEOUS MEDIUM

BY

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INTERNATIONAL ISLAMIC UNIVERSITY MALAYSIA

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ABSTRACT

Heavy metal toxicity has proven to be a major threat and exhibit a several health risks associated with it. The use of thiosemicarbazone has recently gained interest as potential receptors regarding to the ease of synthetic approach and possess to active chelating sites. Chemosensor is an alternative devices and developed by organic-based that have the ability to recognize metal ion or anion in aqueous medium by displaying colour change upon detection of targeted ion. Therefore, in this research study, we have developed four organic-based chemosensor namely 2-acetylpyrrole thiosemicarbazone (AP1) and 3-acetylpyridine 2-hydroxylphenyl thiosemicarbazone (AP4) for Cu^{2+} recognition meanwhile 3-acetylpyridine thiosemicarbazone (AP2) and 4-aminoacetophenone thiosemicarbazone (AP3) for IO_3^- recognition, respectively. All the chemosensors were favourable to DMSO solvent where they showed the strong interaction binding in solvent-ligand interaction. The results showed that AP1 produced high absorbance in 5:5 ratio with co-solvent, AP4 in 8:2 ratio while AP2 and AP3 shared the same ratio which is 9:1 ratio. Both ligands AP1 and AP4 were good making interaction in pH 7 neutral while AP2 and AP3 were optimum in pH 11 alkali. Interference analysis indicate that chemosensor AP1 - AP4 did not involve in any interference from other tested metal ions and anions. The interaction of all the ligand complex had clearly observed on its respected wavelength and the colour for all ligand complex were also successfully changed upon the recognition of metal ion and anion. The experimental data had identified the AP1 chemosensor coordinates Cu^{2+} ion in 1:1 stoichiometry, while AP4 is in 2:1 stoichiometry. In other hand, AP2 and AP3 coordinates IO_3^- showed the 2:1 stoichiometry for both chemosensor. Using computational study of COSMO-RS, it showed the compatibility of AP1 - AP4 with the solvent DMSO through hydrogen bonding interaction. The DFT study and calculations were conducted to analyse the stability of the formation of energy complex and their stability. The application of the chemosensor AP1-AP4 towards environmental samples, which were distilled water, tap water and lake water were successfully showed the positive results in recognition of Cu^{2+} and IO_3^- ion. In this study, the detection limit of chemosensor AP1 was determined at 41.8 µM and at 67.9 µM for AP4. Moreover, the detection limit of AP2 and AP3 chemosensor were determined at 114 µM and 788 µM, respectively. Thus, all respective thiosemicarbazone-based chemosensor were successfully able to make a recognition for aqueous Cu^{2+} and IO_3^- ions as they can served as affordable, portable, convenient and can used as off-site device.

خلاصة البحث

تشكل سمية المعادن الثقيلة تهديدا كبيرا لدورها في العديد من المخاطر الصحية. شاع استخدام الثيوسيميكاربزون مؤخرا كمستقبلات واعدة وذلك لسهولة الطريقة الاصطناعية واحتوائها على مواقع ممخلبة نشطة. المستشعرات الكيميائية هي أدوات بديلة مطورة عضويا له القدرة على التعرف على الأيونات المعدنية أو الأنيونات في وسط مائي عن طريق عرض تغيرات في اللون عند اكتشاف الأيونات المستهدفة. تم في هذه البحث تطوير أربعة مستشعرات كيميائية عضوية وهي: 2-أسيتيلبيرول ثيوسيميكابازون (AP1) و 3-أسيتيلبيريدين 2-هيدروكسيلفينيل ثيوسيميكابازون (AP4) لاستشعار Cu^{2+}، و 3-أسيتيلبيريدين ثيوسيميكابازون (AP2) و 4-أمينو أسيتوفينون ثيوسيميكابازون (AP3) لاستشعار IO_3^-. فضلت جميع المستشعرات مذيب الـ DMSO حيث أظهرت ارتباطات تفاعل قوية في تفاعلات المذيب والرابط. أظهرت النتائج أن AP1 قد أنتج نسبة امتصاص عالية بنسبة 5:5 مع المذيب المشترك، وكان AP4 بنسبة 8:2 بينما كان لـ AP2 و AP3 نفس النسبة وهي نسبة 9:1. كانت لدى كلا الرابطتين AP1 و AP4 تفاعلا جيدا في درجة الحموضة 7 المحايدة، بينما AP2 و AP3 كانتا المثلى في درجة pH 11 القلوية. أشار تحليل التداخل إلى عدم إنتاج AP1-AP4 لأي تداخل للأيونات والأنيونات المعدنية المختبرة الأخرى. لوحظ تفاعل كل مركبات الرابطات بوضوح على طول موجته، وبالتالي تم أيضا تغير لون جميع مركبات الرابطات بنجاح حيث تم استشعار وجود أيون معدني أو أنيون. حددت البيانات التجريبية إحداثيات AP1 المستشعر الكيميائي لأيون Cu^{2+} في ستكيومترية 1:1، بينما كان AP4 في ستكيومترية 2:1، وأظهرت إحداثيات AP2 و AP3 لـ IO_3^- ستكيومترية 2:1 لكلاهما. أظهرت الدراسة الحسابية لـ COSMO-RS توافق AP1-AP4 مع الـ DMSO من خلال تفاعل ارتباط الهيدروجين. تم إجراء دراسة وحسابات الـ DFT لتحليل ثبات تكوين مجمع الطاقة واستقرارها. أظهر تطبيق AP1-AP4 على العينات البيئية (الماء المقطر، وماء الصنبور، وماء البحيرة) نتائج إيجابية في الكشف عن Cu^{2+} و IO_3^-. تم أيضا تحديد حد الاستشعار لـ AP1 عند 41.8 ميكرومتر، ولـ AP4 عند 67.9 ميكرومتر، ولـ AP2 عند 114 ميكرومتر، ولـ AP3 عند 788 ميكرومتر. وهكذا تمكنت جميع المستشعرات الكيميائية المعتمدة على الثيوسيميكابازون من الكشف بنجاح على أيونات Cu^{2+} و IO_3^- المائية، حيث تعتبر هذه المستشعرات الكيميائية رخيصة، ومحمولة، وسهلة الاستعمال، وبالامكان استخدامها كجهاز ميداني.

APPROVAL PAGE

I certify that I have supervised and read this study and that in my opinion, it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a thesis for the degree of Master of Science (Biosciences).

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DECLARATION

I hereby declare that this thesis is the result of my own investigations, except where otherwise stated. I also declare that it has not been previously or concurrently submitted as a whole for any other degrees at IIUM or other institutions.

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All of my hard works is dedicated to my beloved husband, parents, family and friends for all their kindness, love and continuous support.

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Percentage of element CHNSO (%)	$\%\ \text{of element} = \frac{\text{Relative atomic mass (respetive atom)}}{\text{Relative molecular mass (total MW)}} \times 100\%$	88
Limit of detection	$C_{DL} = 3\ \delta/K$	118
Fukui function for nucleophilic attack	$f_k^+ = [q(N + 1) - q(N)]$ for nucleophilic attack	135,179
Fukui function for electrophilic attack	$f_k^- = [q(N) - q(N - 1)]$ for electrophilic attack	135,179
Fukui function for radical attack	$f_k^0 = 1 / 2[q(N + 1) - q(N - 1)]$ for radical attack	135,179

LIST OF SYMBOLS

%	percentage
°C	degree Celcius
π	pi
nm	nanometers
σ	sigma
eV	electron Volt
mL	millilitres
g	gram
λmax	maximum wavelength
M	molar
µM	micro molar
mM	millimolar
g/mol	gram per mol
LOD	limit of detection
δ	standard deviation
K	slope of calibration curve
Å	angstrom
e/Å2	charge density
ΔE	energy gap
a.u.	atomic unit
R2	coefficient determination
ppm	parts per million

LIST OF ABBREVIATIONS

AAS	Atomic absorption spectroscopy	H_2O	Water
ICP-MS	Inductively coupled plasma mass spectrometry	UV-VIS	Ultraviolet–visible spectroscopy
ICC	Indian Childhood Cirrhosis	COSMO-RS	Conductor like Screening Model for Real Solvents
DFT	Density function theory	MEP	Molecular Electrostatic Potential
DNA	Deoxyribonucleic acid	HOMO	Highest occupied molecular orbital
DMSO	Dimethyl sulfoxide	LUMO	Lowest unoccupied molecular orbital
DCM	Dichloromethane	B3LYP	Becke, 3-parameter, Lee-Yang Parr

CHAPTER ONE

INTRODUCTION

1.1 RESEARCH BACKGROUND

In the vast developing area, the environmental pollution from heavy metals has become one of the most important focuses in the world. Heavy metals are highly associated with human life from several centuries. Transition metal ions play critical roles in various biological, industrial and environmental processes (Tavallali et al., 2016). These metal ions are crucial element that present in our earth. These metals present from the natural components of the earth's crust which also can be found at surrounding for instance soil, water and also atmosphere that can lead environmental contamination. Nowadays, heavy metals can be found in distinct area of field such as pharmaceuticals, cosmetics, food industry and also water supply treatment.

Metal ions are categorized as essential and non-essential and which are diverged based on their importance and essentiality towards human and living things. Heavy metals are known as metals and semi-metals have relative potential towards toxicity which may cause to earth's pollution. The unethical activities like industrial production, domestic and also agricultural use by these heavy metals are from human activities itself. However, there are also some metals that contain acute elements for asserting human biological activities such as copper, iron, manganese and zinc. Cobalt, chromium, magnesium, nickel are known as essential nutrients that are required for many biochemical and physiological functions in human body system (Tchounwou et al., 2012).