ADSORPTION OF RHODAMINE B BY SULFOCALIX[4]ARENE THIN FILMS FOR DYE REMOVAL APPLICATION

FARISH ARMANI BIN HAMIDON

SULTAN IDRIS EDUCATION UNIVERSITY

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ABSTRACT

This study investigates the potential of Sulfocalix[4]arene (SC[4]) thin film for the removal and molecular-level adsorption of Rhodamine B dye (RhB), focusing on its performance in extraction and adherence. SC[4] thin films with 5, 10, 15, and 20 layers were fabricated using the spin coating method and subsequently characterised for its optical and topographical properties. Optical characterisation using Ultraviolet-Visible Spectroscopy (UV-Vis) at wavelengths from 260 to 300 nm revealed a progressive increase in absorbance across layers, notably at 277 nm and 283 nm peaks. Topographical analysis was conducted using Atomic Force Microscopy (AFM) to determine thickness and surface roughness. Results indicated a linear correlation between film thickness and the number of layers, with measurements of 58.175 nm for 5 layers, 77.626 nm for 10 layers, 84.608 nm for 15 layers, and 94.806 nm for 20 layers. Surface roughness, quantified via root mean square roughness (R_q), was significantly influenced by the number of layers. Adsorption studies of SC[4] thin films immersed in RhB dye solutions, characterised by UV-Vis, indicated that adsorption is the primary mechanism, evidenced by consistent, stable absorbance and dye concentration under both dark and visible light environments. The films demonstrated stable adsorption without prompting degradation of the RhB solution. Thicker films exposed to visible light showed a slight decrease in absorbance over time, suggesting environmental factors could affect adsorption depending on film thickness. A slight redshift in RhB's absorption peak from 554 to 560 nm on SC[4] surfaces, along with a gradual increase in absorbance over immersion time, implies effective adsorption driven by Van der Waals forces. Among the examined thin films, the 5-layer SC[4] film demonstrated the most effective performance, providing reliable adsorption capability and stability under diverse light environments. These findings highlight the potential of SC[4] thin films as efficient adsorbents for RhB dye removal from textile wastewater.

PENJERAPAN RHODAMIN B OLEH SELAPUT NIPIS SULFOKALIKS[4]ARENA UNTUK APLIKASI PENYINGKIRAN PEWARNA

ABSTRAK

Kajian ini telah menyiasat keupayaan selaput nipis Sulfokaliks[4]arena (SC[4]) bagi penyingkiran dan penjerapan molekul Rhodamine B (RhB) pada skala molekul, dengan tumpuan terhadap keberkesanannya dalam proses pengekstrakan dan pelekatan. Selaput nipis SC[4] dengan 5, 10, 15, dan 20 lapisan telah dihasilkan menggunakan kaedah salutan berputar dan seterusnya telah dicirikan untuk mendapatkan sifat optik dan topografinya. Pencirian optik menggunakan Spektroskopi Cahaya Tampak-Ultralembayung (UV-Vis) pada panjang gelombang antara 260 hingga 300 nm menunjukkan peningkatan serapan cahaya terutama pada puncak 277 nm dan 283 nm seiring dengan bilangan lapisan. Analisis topografi menggunakan Mikroskopi Daya Atomik (AFM) dijalankan untuk menentukan ketebalan dan kekasaran permukaan filem. Hasil kajian menunjukkan hubungan linear antara ketebalan selaput dengan bilangan lapisan, dengan ukuran ketebalan sebanyak 58.175 nm untuk 5 lapisan, 77.626 nm untuk 10 lapisan, 84.608 nm untuk 15 lapisan, dan 94.806 nm untuk 20 lapisan. Kekasaran permukaan, yang dihitung melalui nilai punca purata kuasa dua kekasaran (R_q), turut didapati sangat dipengaruhi oleh bilangan lapisan. Kajian penjerapan selaput nipis SC[4] yang direndam di dalam larutan pewarna RhB dan dicirikan menggunakan UV-Vis menunjukkan bahawa penjerapan merupakan mekanisme utama, seperti yang dibuktikan melalui serapan cahaya dan kepekatan pewarna yang stabil dan konsisten di bawah keadaan cahaya gelap dan cahaya tampak. Selaput nipis ini menunjukkan kestabilan penjerapan tanpa mencetuskan kelunturan larutan RhB. Selaput yang lebih tebal yang terdedah kepada cahaya tampak menunjukkan sedikit penurunan dalam serapan cahaya dari semasa ke semasa, mencadangkan bahawa faktor persekitaran boleh mempengaruhi penjerapan bergantung pada ketebalan filem. Sedikit peralihan puncak serapan RhB dari 554 ke 560 nm pada permukaan SC[4], bersama dengan peningkatan beransur-ansur dalam serapan cahaya sepanjang tempoh rendaman, menunjukkan penjerapan yang berkesan didorong oleh daya Van der Waals. Antara selaput nipis yang diuji, selaput nipis SC[4] 5-lapisan menunjukkan prestasi yang paling berkesan, dengan keupayaan penjerapan yang boleh dipercayai serta kestabilan dalam pelbagai persekitaran pencahayaan. Hasil penemuan kajian berjaya membuktikan keupayaan selaput nipis SC[4] sebagai penjerap yang berkesan untuk penyingkiran pewarna RhB daripada air sisa tekstil.

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LIST OF ABBREVIATIONS

A	Absorbance
AFM	Atomic Force Microscopy
BOD	Biological Oxygen Demand
C	Carbon
C[4]	Calix[4]arene
CPK	Corey-Pauling-Koltun Model
CVD	Chemical Vapor Deposition
DFT	Density Functional Theory
DO	Dissolve Oxygen
N	Nitrogen
PAMAM	Polyamidoamine
PPI	Polypropylene Imine
PVD	Physical Vapor Deposition
RHB	Rhodamine B
SC[4]	4-Sulfocalix[4]arene
SDG	Sustainable Development Goal
UV	Ultraviolet
UV-Vis	Ultraviolet-Visible Spectroscopy
VDW	Van Der Waals
VSEPR	Valence Shell Electron Repulsion Theory

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LIST OF SYMBOLS

E_g	Band Gap Energy
R_q	Root Mean Square Roughness
ΔY	Height Variation or Thickness of Thin Film
λ_{max}	Maximum Absorbance Wavelength
μ	Statistical Mean
σ	Statistical Standard Deviation
ε	Molar Absorptivity

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CHAPTER 1

INTRODUCTION

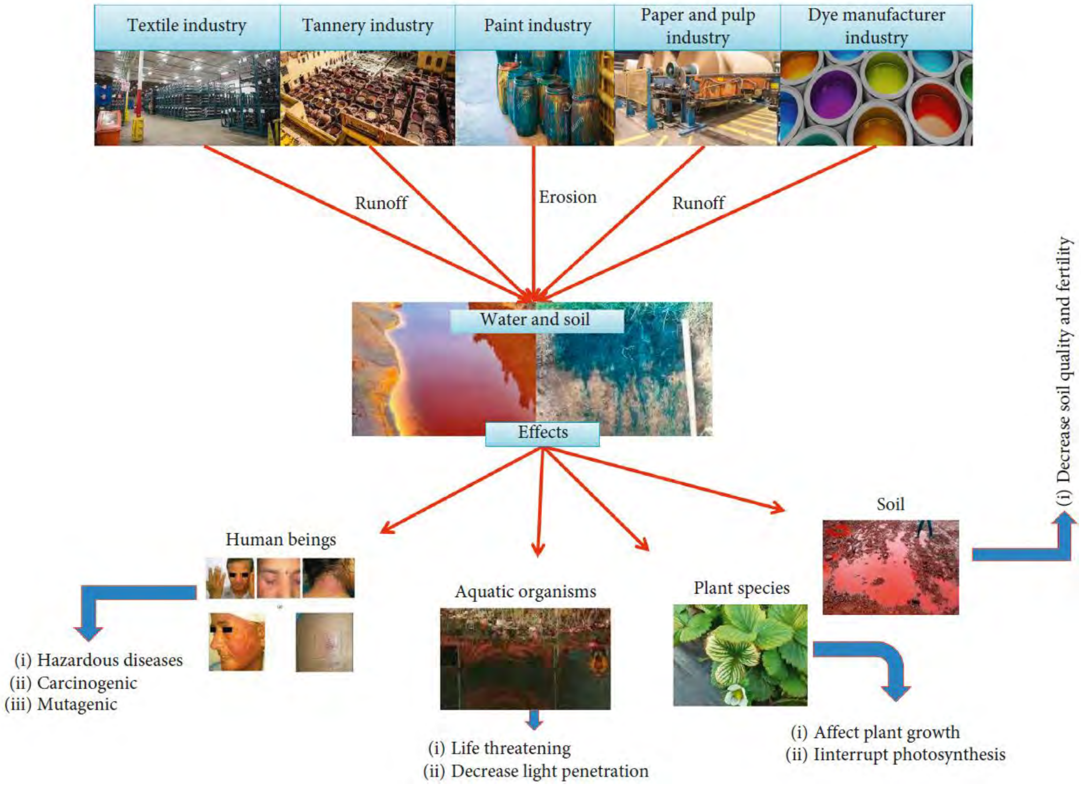
1.1 Research Background

The industrial use of dyes has increased dramatically in recent decades, particularly in the textile industry. **Figure 1.1** shows the threats caused by various industries towards human health and the environment within the textile industry (Al-Tohamy et al., 2022; Ayele et al., 2021; Kaushal et al., 2021). Dyes are hazardous, and even minute doses can cause significant harm to human health as it can cause asthma, rhinitis and dermatitis with prolonged exposure (Ho et al., 2005; Sardar et al., 2021). It poses a hazard to marine life in aquatic ecosystems due to its depletion of dissolved oxygen (DO), impacts on pH and salinity, and light attenuation (Sardar et al., 2021).

In recent news, in 2024, 25 out of 672 rivers in Malaysia were categorised as contaminated, with Class 3 and 4 quality ratings. This classification was predominantly due to industrial activities, effluent treatment, agriculture, urbanisation, and animal farming. The report revealed that 72% of the examined rivers were clean, while 24% were moderately polluted (Bernama, 2024; M. I. Ibrahim, 2024). The 2021 news report also emphasised the bright red floods resulting from *batik* dye release from textile factories, prompting public concern. The local authorities clarified that the red colour of the water was the result of dye discharge, a phenomenon that is prevalent in regions that are known for their traditional dyeing processes (Agensi, 2021).

Figure 1.1

The Environmental Damage Contributed by Synthetic Dyes from Several Industries

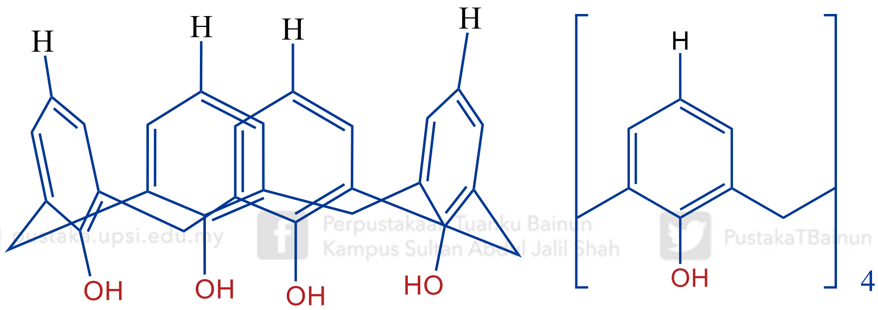


(Ayele et al., 2021)

Calixarenes are excellent molecular platforms for the complexation of metal ions due to its rigid structures, shown in **Figure 1.2** (S. Patra et al., 2012). Modifications can be made to the lower and upper rims of the calixarenes, and the modified calixarenes have a highly organised structure to form binding sites (Mokhtari et al., 2011a, 2011b; Mokhtari & Pourabdollah, 2012a). Through interactions with the aromatic rings and hydrogen bonds, the calixarene molecule can react with various types of guest molecules due to the presence of upper and lower rims. Altering these upper and lower rims will improve the selectivity of calixarene for distinct target users, whether by raising or reducing the phenolic units (Cen et al., 2022; Legnani et al., 2015; Murphy et al., 2015; Zhou et al., 2013).

Figure 1.2

Schematic Representation of the Core Calix[4]arene Structure that will be used in this Work



1.2 Problem Statement

This study is motivated by the urgent need to address industrial textile dye pollution, a significant environmental issue threatening water resources, ecosystems and public health. First, the study aligns with the Sustainable Development Goals (SDGs) introduced by the United Nations under the 2030 Agenda (United Nations, 2015). The Sustainable Development Goals provide a comprehensive and global framework for addressing poverty, safeguarding the environment, and promoting peace and prosperity (United Nations, 2015). In particular, it contributes to three of these goals, which are SDG 6 Clean Water and Sanitation, SDG 11 Sustainable Cities and Communities, and SDG 14 Life Below Water (United Nations, 2015).

SDG 6 focuses on ensuring the availability and sustainable management of water and sanitation for all. It addresses critical issues such as water scarcity, water pollution, and inadequate sanitation, which threaten billions of people, human health, and environmental sustainability (United Nations, 2015). Despite progress, billions still lack and are beyond reach safe, managed drinking water and sanitation in rural and urban areas. Simultaneously, the wetland ecosystems, crucial to water purification, flood regulations, and biodiversity, confront serious threats from pollution, climate change, and overexploitation. Wetland habitats have experienced a concerning 85% decline over the last three centuries, and since 1970, 81% of inland wetlands have also declined, with many now facing the threat of extinction. Extensive conservation and rehabilitation are essential to preserve these vital ecosystems (United Nations, 2015, 2023).

Next is SDG 11, which aims to make cities and human settlements inclusive, safe, resilient, and sustainable. This goal highlights the importance of improving living conditions in urban areas by addressing environmental challenges such as poor air quality, unmanaged waste, and pollution that threaten public health and well-being (United Nations, 2015, 2023). Even though SDG 11 does not specifically target the environmental problems caused by factories and industries such as textiles, the adverse impacts of these industrial activities on residential areas and local settlements can indirectly affect the people in both urban and rural settings. This aligns with the intention of SDG 11, particularly Target 11.6, which focuses on reducing the environmental impact of cities, with special attention to improving air quality and managing municipal and industrial waste.

Finally, SDG 14 focuses on conserving and sustainably using the oceans, seas, and marine resources. It addresses critical issues such as marine pollution, ocean acidification, overfishing, and the degradation of marine ecosystems, all of which are vital for the health of the planet and the well-being of millions of people (United Nations, 2015, 2023). Coastal eutrophication poses a growing threat to marine ecosystems and communities. This is mainly driven by human activities such as agriculture and aquaculture, and wastewater discharges, which contribute to nutrient loading in coastal areas (United Nations, 2023). The result is widespread algal blooms that deplete oxygen levels, harm marine life, contaminate seafood, and damage ecosystems such as seagrass beds and coral reefs. The impacts have severe consequences for marine ecosystem health, local communities, fisheries and tourism (United Nations, 2023). While natural blooms can sprout due to natural processes, such as the upwelling of nutrient-rich or low-flow waters, human activities are the main driving force behind the increasing frequency, duration and extent of eutrophication. With the added challenge of climate change and its complex interactions with a warming ocean, worsening these impacts is expected (United Nations, 2015, 2023).

Next, there are multiple significant challenges associated with the use of dyes in the textile industry, overwhelmingly associated with health and environmental issues. Despite its indisputable significance, the industry consumes a substantial quantity of fuel and chemicals and is one of the most significant worldwide contaminants (S. C. Bhatia, 2017). Those dyes frequently used in textile manufacturing are considered sensitisers that can induce allergic reactions, especially among individuals with pre-existing atopic conditions or those exposed to synthetic materials. In addition, the chemical composition of numerous dyes frequently includes carcinogenic and toxic substances, posing substantial risks to both consumers and workers (Ho et al., 2005; Jenkins, 1978; Lewis et al., 2017; Ryberg et al., 2009; Sardar et al., 2021; Uddin, 2021).

The environmental pollution caused by the inefficient treatment of wastewater from dyeing processes results in the discharge of vast volumes of lucidly coloured effluent into public sewers and waterways, which contain these hazardous materials (Azanaw et al., 2022; Bharagava et al., 2018; A. Khatri & White, 2015; Lewis et al., 2017; Sarker et al., 2019). The industry’s dependence on conventional dyeing techniques further exacerbates the environmental burden, emphasising the necessity of sustainable technologies and cleaner manufacturing processes (A. Khatri & White, 2015). Given the combined potential health hazards and environmental impacts, the textile industry's dyeing materials demand an urgent need for more secure alternatives and stringent supervision and extraction associated with these dyes.

Waste disposal poses intricate challenges for a wide range of industrial sectors, particularly considering the substantial expenditures related to regulating the vast amounts of waste created. Illegal dumping on barren land and roadsides is a common consequence of insufficient waste management, particularly in developing countries (P. P. Singh & Ambika, 2022). The textile industry generates vast volumes of lucidly coloured effluent, including numerous toxic, persistent dyes that contaminate aquatic ecosystems. The textile industry generates an enormous amount of lucidly coloured effluent that consists of numerous types of toxic, persistent dyes and pigments that contaminate aquatic ecosystems.

A synthetic dye that is extensively employed in the textile industry, Rhodamine B (RhB) is of particular concern due to its substantial environmental and health impacts. Research has shown that it has toxic effects, with some studies implying that it could possess carcinogenic properties, particularly at higher concentrations (Abdul Razak & Rohani, 2018; Rabti et al., 2019; Uddin, 2021). This raises noticeable concerns regarding the possibility of long-term exposure threats to both humans and aquatic life. Examples include severe eye damage risk and harmful irritations triggered upon skin contact or ingestion. It is also reported to be harmful upon skin contact or ingestion irritations and severe eye damage risk (Rabti et al., 2019).

RhB is frequently detected in the hazardous effluents released during textile dyeing processes, which frequently contain a combination of toxic, carcinogenic, and mutagenic compounds. The fundamental necessity for raised environmental management is emphasised by the persistence of those substances in water supplies, as it have the potential to adversely impact water quality. It is crucial to address the environmental impact of RhB in order to establish sustainable textile manufacturing practices (Lewis et al., 2017).

Hence, given these challenges, this study is essential as it explores the potential of calixarenes, a non-toxic organic material, for detecting cations in aqueous environments. Due to this potential, RhB served as a guest molecule to be adsorbed by sulfocalix[4]arene (SC[4]) thin films fabricated by using the spin coating method, with the goal of exploring its application in dye removal processes.

1.3 Research Motivation

The research centres on the potential of calixarene molecules, specifically, SC[4], as host-guest systems. This is due to its adaptable, versatile and modifiable structure, which renders it appropriate for a variety of applications, including sensors and adsorbents (Eddaif et al., 2019; Sanabria Español & Maldonado, 2019). The purpose of the study is to investigate the potential of SC[4] as a cost-effective and efficient solution to the problems associated with dye removal from textile effluent. The textile industry, which constitutes one of the largest consumers of water, generates substantial amounts of effluent contaminated with hazardous chemicals and dyes, such as RhB. The objective of this study is to advance the comprehension of host-guest interactions in calixarene chemistry and to develop a novel, eco-friendly technology for the removal of RhB dye from textile wastewater in accordance with the environmental concerns associated with wastewater from the textile industry.

1.4 Research Objectives

This study focuses on several objectives that need to be achieved, which are:

1) To investigate the optical properties and band gap energy of spin-coated 4-sulfocalix[4]arene (SC[4]) thin films using UV-Visible spectroscopy and the Tauc-Plot method.
2) To measure the thicknesses and surface topography analysis of SC[4] thin films using an Atomic Force Microscope (AFM).
3) To evaluate the adsorption performance of SC[4] thin films with different thicknesses by analysing RhB dye concentration over time.

1.5 Research Scope and Limitations

This study centres on the fabrication of a calixarene derivative thin film, SC[4] (host), using the spin coating method with RhB (guest). The main aim is to investigate the potential of this thin film for natural dye removal at the molecular level and to evaluate its performance in dye extraction and adherence.

The characterisation of SC[4] thin films focused on its optical and topographical properties. Thin films comprising 5, 10, 15, and 20 layers of SC[4] were characterised.

The adsorption study of SC[4] thin films involving RhB dyes was confined to an investigation using UV-Vis spectroscopy (UV-Vis) to ascertain trends in dye adsorption. Financial constraints and time restrictions restricted the capacity to conduct a more comprehensive investigation using more extensive characterisation techniques, including Fourier-Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Field Emission Scanning Electron Microscopy (FESEM), and Atomic Force Microscopy (AFM).

Although the characterisation was restricted to UV-Vis, it offered a reliable indication of adsorption by measuring the absorbance of dye molecules on the surfaces of thin films. This method allowed a thorough analysis of interfacial coatings and provided insights into molecular interactions at the surface level. However, it is crucial to acknowledge that certain constraints such as optical properties, thickness of the coatings, and adsorbate characteristics could influence measurement accuracy. Additionally, the complexities of the adsorption process, including molecular orientation and layer configuration, may impact the precision. Regardless of these constraints, UV-Vis continues to be a feasible and effective technique for evaluating pollutant removal, as dye molecules adhere to the thin film surface without degradation.

1.6 Research Novelties

The novelty of this study lies in the innovative and novel utilisation of calixarenes, which have been relatively restricted because of it is hydrophobic nature and low water solubility. This study overcomes these limitations by employing water-soluble calixarene derivatives, previously synthesised by other researchers, while demonstrating its unique ability to form stable complexes with inorganic guest molecules. This remarkable property unlocks new potential for diverse applications, particularly in molecular recognition, sensing, and supramolecular chemistry, making it highly promising for advanced scientific and industrial applications.

Moreover, by broadening and diversifying the functional applications of calixarene-dye systems derivatives, this work creates new opportunities for environmentally sustainable solutions. By advancing beyond traditional host-guest chemistry, it provides groundbreaking insights into wastewater treatment and dye removal, significantly expanding the utility of these materials.

1.7 Summary of the Whole Thesis

This thesis has five distinct chapters, each focusing on a particular aspect of the study. The structure ensures a coherent flow of ideas, enabling the audience to comprehend the study's progression with clarity. The project commences with an introduction to the hosts and guests, highlighting its importance in addressing the difficulties confronting the textile sector. It systematically navigates the experimental procedures and results, culminating in a comprehensive analysis of calixarene thin films fabricated via the spin-coating technique and its application in RhB dye adsorption investigations. The thesis culminates in comprehensive recommendations and insights derived from this study.

Chapter 1 introduces the foundational concepts of solid-state physics and thin films, highlighting the unique properties that distinguish thin films from bulk materials. It then explores the environmental challenges posed by industrial dyes, particularly RhB, used in the textile industry and its harmful impacts on ecosystems and human health. Highlighting the potential of SC[4] in its thin film form fabricated via the spin-coating method as an innovative material for sustainable dye removal, the chapter outlines the study's objectives, scope, limitations, and novel contributions to environmental remediation and nanotechnology.

Chapter 2 explores the key concepts and techniques in material characterisation and surface interactions. It begins by introducing adsorption and calixarene as host-guest molecules, emphasising its significance in material science and molecular interactions. The chapter also explores molecular modelling, hydrocarbon properties, and the environmental impact of textiles, emphasising the role and relevance of these factors in sustainable applications. Additionally, it discusses the use of host-guest molecules in textile industries, the application of spin coating techniques for thin film fabrication, and the characterisation methods explicitly focusing on the optical and topographical properties using Ultraviolet-Visible Spectroscopy and Atomic Force Microscopy to evaluate film characteristics investigated in this study.

Chapter 3 provides an overview of the materials and methods used in this study, with the experimental procedures derived from previous works outlined in the literature review and subsequently carried out. Specific details regarding the fabrication of SC[4] films, experimental characterisations, and adsorption investigations are outlined, and each stage of the experiment, along with the associated analytical calculations, is thoroughly described. The experimental procedures were conducted under appropriate parameters and environments, and its rationale was explained. A comprehensive discussion of the findings from these studies is presented in Chapter 4.

Next, Chapter 4 presents and discusses the results following the data collection and experimentation. Initially, the molecular modelling of the SC[4] molecule was performed using the CPK model and statistical comparisons with the DFT computation, which were then presented and described. After the deposition of materials onto the substrates using the spin-coating technique, the optical properties and topographical analysis of the deposited thin film samples were investigated using UV-Vis and AFM were investigated and presented. UV-Vis solution characterisation studies for C[4] and

SC[4] were conducted to analyse any differences between the two, with the results displayed accordingly. The results of the adsorption study of RhB by SC[4] were also described in detail, highlighting the impacts of film thickness and environmental factors, which were thoroughly examined and clearly presented. All data were presented in the form of tables and graphs in accordance with its particular relevance and appropriateness to each situation.

Finally, Chapter 5 covers the conclusions and recommendations of this study based on the evidence gathered through the experiments and analysis. This chapter concluded the research, offering insights and recommendations for future studies on the adsorption properties of calixarene and its derivatives, paving the way for further exploration by other researchers.