

**THE USE OF LOW COST ZEOLITES FOR THE REMOVAL OF  
SELECTED CONTAMINANTS AND COMBINATION WITH BIOLOGICAL  
PROCESS FOR WASTEWATER TREATMENT**

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*To my beloved mother, father, brother and sisters*

## ACKNOWLEDGEMENT

I would like to thank my supervisor Prof. Dr. Alias Mohd. Yusof for giving me the chance to work on his project as well as for his valuable guidance, support and untiring patience.

I am grateful to Associate Professor Dr. Zaharah Ibrahim, Dr. Zaiton Abdul Majid and Professor Dr. Noor Aini bt. Abdul Rashid for their constant vigilance and valuable suggestions throughout this study. I would also express my appreciation to all other faculty members and staff in the Department of Chemistry and Department of Biology for their enormous help with my study.

I thank all of my friends, colleagues and laboratory personnel who extended their time, expertise, generous advice, criticism, technical assistance and encouragement during my research. I like to acknowledge everyone, but I am to be constrained to a few in mentioning names as Mr. Ayob Jabal, Mr. Hanan Basri, Mr. Azmi M. Rais, Mrs. Z. Ain Jalil, Mr. Hj. Yasin bin. M. Sirin, Miss. Nurul H. Sapiren, Mr. M. Nazri Zainal, Mr. Dinda Hairul, Mr. Hamzah, Mr. Abdul Kadir, Mrs. Mek zum, Mr. Amin Derani, Mr. Abdur Rahim, Mrs. Mariam Hassan, Mr. Azani b. Ishak of Department of Chemistry, Mr. Awang, Mrs. Fatimah, Mrs. Radiah and who indebted me most for their assistance in pursuing laboratory work.

I owe thanks to my all family members, my mother, brothers and sisters for their help and love without that I cannot continue my study here.

## ABSTRACT

Two types of low cost zeolites, namely natural mordenite and synthetic zeolite Y synthesized from a local agro-wastes, rice husk ash were applied to remove various types of contaminants from water. Zeolite Y was synthesized under hydrothermal conditions with appropriate seeding and aging methods, in which the overall relative composition of  $\text{Na}_2\text{O}$ :  $\text{Al}_2\text{O}_3$ :  $\text{SiO}_2$ :  $\text{H}_2\text{O}$  is 5.1: 1.0: 10.5: 184.0. The physico-chemical properties of the zeolites were characterized using various techniques. Ammonium removal studies were carried out with the raw mordenite and as-synthesized zeolite Y. Pseudo first order kinetic model and pseudo second order kinetic model were employed to understand the sorption kinetics, while several isotherm equations such as Langmuir, Freundlich and Temkin to study the sorption behavior. To bombard against oxyanions such as nitrate, sulfate and phosphate, the surface chemistry of the zeolites were altered by a cationic surfactant, quaternary amine HDTMA-Br in proportional to the external cation exchange capacity of the zeolites. Both the surfactant-modified zeolites (SMZ) presented significant affinity and adsorption capacity towards the oxyanions. Besides that, while the unmodified zeolites had no affinity towards anionic organic, Acid Orange 7 (AO7), the SMZ showed impressively high adsorption capacity with a rapid removal rate. Suitable kinetics and isotherms models were employed to further understand the sorption behaviors. Combination of the adsorption and biological treatment process in wastewater treatment is interesting. Prior to the study of the combined process, the powdered zeolites and its modified form were first fabricated to the small round particle; several studies were carried out to study the physico-chemical characteristics of the zeolite particles. Indigenous bacteria strains were isolated from a wastewater source and the performance of the bacteria to remove different contaminants was screened. Finally the use of zeolite particle in textile wastewater treatment together with the mixed cultures of bacteria was studied in several approaches.

## ABSTRAK

Dua jenis zeolit kos rendah, iaitu zeolit semula jadi mordenit dan zeolit Y sintetik yang disintesis daripada sisa pertanian tempatan, iaitu abu sekam padi telah digunakan untuk menyingkirkan beberapa jenis pencemar daripada air. Zeolit Y yang disintesis dalam keadaan hidro-terma dengan kaedah pembenihan dan penungguan, dengan kandungan keseluruhan bagi  $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{H}_2\text{O}$  ialah 5.1: 1.0: 10.5: 184.0. Ciri-ciri fizikal-kimia zeolit tersebut telah diperiksa dengan pelbagai kaedah. Kajian penyingkiran ammonium telah dijalankan dengan mordenit dan zeolit Y. Model pseudo kinetik tertib pertama dan model pseudo kinetik kedua digunakan untuk meneliti kinetik penjerapan, sementara itu beberapa jenis persamaan isoterma seperti Langmuir, Freundlich dan Temkin digunakan untuk meneliti kelakuan penjerapan. Demi menjerap oksi-anion seperti nitrat, sulfat dan fosfat, kimia permukaan zeolit tersebut perlu ditukarsuai dengan surfaktan kation, heksadesiltrimetil ammonium (HDTMA-Br) dengan kandungan berkadar dengan kapasiti penukaran kation luar. Kedua-dua zeolit ditukarsuai surfaktant (SMZ) menunjukkan afiniti yang jelas dan kapasiti penjerapan terhadap oksi-anion. Sementara zeolit asli tiada afiniti terhadap organik anionik, Oren Asid 7 (AO7), SMZ menunjukkan kapasiti penjerapan tinggi yang memerangsangkan dengan kadar penyingkiran laju. Model kinetik dan isoterma yang bersesuaian telah digunakan untuk memahami kelakuan penjerapan tersebut. Gabungan penjerapan dan rawatan biologi dalam rawatan air sisa adalah suatu proses yang menarik. Sebelum kajian proses gabungan itu, zeolit dalam bentuk serbuk dan SMZ telah dibentuk kepada bebola kecil; beberapa kajian telah dijalankan untuk memeriksa ciri-ciri bebola zeolit tersebut. Bakteria tempatan telah dipisah daripada sumber air sisa dan keupayaan bakteria-bakteria itu untuk menyingkir pelbagai pencemar telah diuji. Akhirnya, penggunaan bebola zeolit dalam rawatan sisa air tekstil bersama dengan campuran bakteria dalam beberapa pendekatan telah dikaji.

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## LIST OF SYMBOLS

°C	-	Degree Celsius
C <sub>o</sub>	-	Initial concentration
C <sub>e</sub>	-	Equilibrium concentration
cm	-	Centi meter
dm	-	Deci meter
g	-	Gram
h	-	Hour
kg	-	Kilo gram
kJ	-	Kilo Joule
kPa	-	Kilo Pascal
kV	-	Kilo Volt
L	-	Liter
lb	-	Pound
m	-	Meter
M	-	Molar
mA	-	Mili ampere
meq	-	Mili equivalent
mg	-	Mili gram
min	-	Minute
mL	-	Mili Liter
mm	-	Mili meter
mmol	-	Mili mol
N	-	Normal
nm	-	Nano meter
ppm	-	Part per million

ppb	-	Part per billion
rpm	-	Revolutions per minute
Å	-	Angstrom
µg	-	Micro gram
µm	-	Micro meter
µL	-	Micro Liter

## LIST OF ABBREVIATIONS

AAS	-	Atomic Absorption Spectroscopy
ADMI	-	American Dye Manufacturers Institute
AlPO <sub>4</sub>	-	Aluminophosphates
ANA	-	Analcime
AO7	-	Acid Orange 7
ASAP	-	Accelerated Surface Area and Porosimeter
APHA	-	American Public Health Association
BEA	-	Zeolite Beta
BET	-	Brunauer, Emmet, and Teller
BJH	-	Barrett-Joyner-Halenda
BTEX	-	Benzene, Toluene, Ethylene and Xylene
CCA	-	Chromated Copper Arsenate
CEC	-	Cation Exchange Capacity
CHA	-	Chabazite
CMC	-	Critical Micelle Concentration
COD	-	Chemical Oxygen Demand
CQ	-	Chloroquin
DDTMA	-	Decadecyltrimethylammonium
DHA	-	Dehydroabietic Acid
DNA	-	Deoxyribonucleic Aid
ECEC	-	External Cation Exchange Capacity
EDAX	-	Energy-Dispersive X-ray Spectroscopy
EDI	-	Edingtonite
EPA	-	Environmental Protection Agency
ERI	-	Erionite

ETFE	-	Ethylenetetrafluoroethylene
FAU	-	Faujasite
FEP	-	Fluorinated Ethylene Propylene
FER	-	Ferrierite
FESEM	-	Field Emission Scanning Electron Microscopy
FT-IR	-	Fourier Transform Infrared
GIS	-	Gismondine
HDTMA	-	Hexadecyltrimethylammonium
HEU	-	Clinoptilolite
ICDD	-	International Centre for Diffraction Data
IIS	-	Ibnu Sina Institute for Fundamental Science Studies
ISO	-	International Organization for Standardization
IUPAC	-	International Union of Pure and Applied Chemistry
IZA	-	International Zeolite Association
LOI	-	Lost of Ignition
LTA	-	Linde Type A
LTL	-	Linde Type L
MeAPO	-	Metal-substituted Aluminophosphates
MER	-	Merlinoite
MFI	-	Zeolite Socony Mobil – five
MOR	-	Mordenite
MTT	-	Zeolite Socony Mobil – twenty-three
PAC	-	Plug Flow Combustor
PDF	-	Powder Data File
PHI	-	Phillipsite
QAC	-	Quaternary Ammonium Compounds
RHA	-	Rice Hush Ash
SAPO	-	Silicoaluminophosphates
SBU	-	Secondary Building Unit
SCF	-	Surface Complex Formation
SIRIM	-	Standards and Industrial Research Institute of Malaysia
SMC	-	Surfactant Modified Clay

SMM	-	Surfactant Modified Mordenite
SMY	-	Surfactant Modified Zeolite Y
SMZ	-	Surfactant Modified Zeolite(s)
SOC	-	Synthetic Organic Chemicals
TDTMA	-	Tetradecyltrimethylammonium
TG-DTA	-	Thermogravimetry-Differential Thermal Analysis
US	-	United States
USA	-	United States of America
UV	-	Ultra Violet
UV-Vis	-	Ultra Violet-Visible
WHO	-	World Health Organization
XRD	-	X-Ray Diffraction
XRF	-	X-Ray Fluorescence
ZSM	-	Zeolite Socony Mobil

## CHAPTER 1

### INTRODUCTION

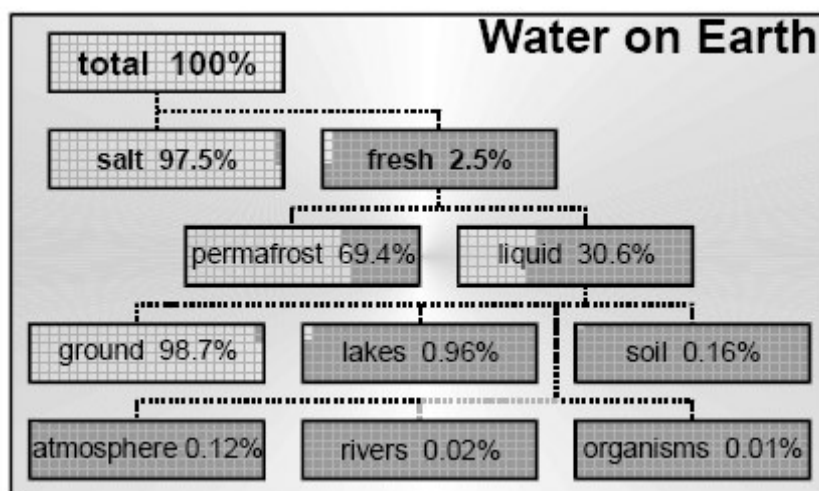
#### 1.1 Background

Water is essential for all life on earth. Including human beings, all life uses water as the basic medium of metabolic functioning. The removal and dilution of most natural and human-made wastes are also accomplished almost entirely by water. In addition, water possesses several unique physical properties that are directly responsible for the evolution of our environment and the life that functions within it. It seems that water is in abundance with two thirds of the planet covered by oceans. However, it is not quantity but quality that counts (Figure 1.1) (Fischer, 2001).

Obviously, humans have been polluting water since the early days of civilization. The development of towns and cities in close proximity to rivers also caused the rivers to become polluted by human waste and effluents. Indeed whole civilization has disappeared not only because of water shortages resulting from changes in the climate but also because of water-borne diseases such as cholera and typhoid (Lee and Speight, 2000). The industrial revolution of nineteenth century, rapid growth in human population has placed strains to environment for instance adding more chemical contaminants into the aquatic system. The presence of a wide range of synthetic organic chemicals (SOC) was confirmed by the Environmental Protection Agency (EPA) of USA in finished drinking water, in many locations, even



those are from ground water supply (Cotruvo *et al.*, 1983). This survey breaks the historical concept of viewing ground water as a relatively uncontaminated resource, unspoiled by the human activities that affect surface waters. The presence of even trace quantities of SOC in finished drinking water should be encountered as a major future threat to the supply water for the existing mechanism of contamination of the source by man-made pollution. Especially in densely populated or industrial areas the quality of water can become a problem. These areas have a high demand of clean water while at the same time produce large amounts of wastewater. Beyond a certain point the natural occurring purification processes are no longer sufficient and ground water quality will start to decrease, causing both environmental and economical problems.



**Figure 1.1:** Overview of all water on earth. The amount of fresh liquid water is less than 1 %.

Concerned for sustaining healthy water resources, the public are calling for more and more environmental restrictions. Consequently, industries and scientists are searching for economic and efficient methods in protecting water resources from pollution. Using the sorption process for the removal of contaminants from wastewater has a relatively shorter history if compared to other water purification processes. The earliest documented use of carbon for the removal of impurities in solutions was made by Lowitz, he observed that charcoal would decolorize many liquids in 1785 (Clark and Lykins, 1989). Nowadays adsorption on activated carbon is a recognized method for the removal of organics and harmful metals from

wastewater while the high cost of activated carbon production and application limits its use in adsorption. A search for low cost and easily available adsorbents has led to the investigation of materials of agricultural and biological origin as potential metal sorbents (Hammaini, *et al.*, 1999).

Zeolites were proven as potential sorbents in aquatic pollution control especially in the removal of water hardness, ammonium and toxic metals. Besides the natural occurring zeolites, the efficiencies of low cost synthetic zeolites in the water treatment have been evaluated. Generally, the sources should have high content of silica or alumina. In addition, these compositions should be highly reactive aiming towards cost-effective synthesis. Mineralogists have studied zeolites for two and half centuries beginning with the first member, stilbite, which was discovered in 1756 (Barrer, 1982). However their applications in industry have been developed only in the last 50 years. The openness of the anionic frameworks ensures the easier mobility both of cations in ion exchangers and of water molecules or other guest species.

Among the available local natural materials, rice husk which contains high percentage of silica has drawn the attention of researchers worldwide. Rice husks are natural sheaths that form on rice grains during their growth; it is a non-biodegradable fibrous material with high silica content. These husks are removed during the refining of rice. The world beneficiation of rice generates as by-product rice husk in significant quantities that corresponds to about 20 % of its initial weight (Della *et al.*, 2002). Among the population consume the rice as main daily food, South and South East Asia countries account for over 90 % of world's rice production (Wang *et al.*, 1998). In Malaysia, rice husk is produced in abundance after rice harvesting season, the annual production of rice leaves behind about 2.4 million tonnes of husk as waste product (Hamdan *et al.*, 1997).

The utilization of RHA as an alternative source of active silica towards the preparation of zeolites has been reported since the early of 1980's by Rao and co-workers (Bajpai *et al.*, 1981; Dalal *et al.*; 1985; Rawtani, 1989). In the pioneering work of Rao's group, several type of zeolites such as mordenite, zeolite NaX and zeolite ZSM-5 have been successfully synthesized. Apart from that, zeolite A and

zeolite Y (Hamdan, 1997), zeolite ZSM-48 (Wang, 1998) were also successfully synthesized. It is trusted that other kinds of zeolite and mesoporous silica will be synthesized from time to time in the light of the early work.

Zeolites possess a net negative structural charge due to the isomorphic substitution of cations in the crystal lattice. Thus, ordinary zeolites have little or no affinity for neutral and anionic solutes. Consequently, in order to treat oxyanions and anionic organic contaminants, the surface chemistry of zeolite was altered by attaching appropriate quaternary ammonium cationic surfactants. At the maximum surfactant sorption, the surfactant molecules form bilayers on zeolite surfaces with the lower layer held by electrostatic interaction between the negatively charged zeolite surfaces and the positively charged surfactant headgroups in both layer. Under the surfactant bilayer configuration, the zeolite reverses its surface charge resulting in a higher affinity for negatively charged anionic contaminants.

Adsorption and biological treatment are two common methods applied in wastewater treatment. In general, these two approaches have been used either separately, but in same process (e.g., an activated sludge treatment followed by adsorption on activated carbon as polishing step), or as an alternative to each other. However, it has also shown that adsorption and biotreatment can be used simultaneously. For example, microorganisms can be used as an adsorbing material (biosorption) as well as active degraders of the target organic compounds (Armenanta *et al.*, 1996). The biomass is first contacted with the wastewater to promote adsorption of the dissolved organics on the surface of microbial flocs prior to biodegradation of the same microorganisms. In such cases, the biomass is also the adsorbing material. In other cases, the adsorbing material may be a sorbent such as zeolite added to a microbial process to improve the overall performance of the system and increase the removal of recalcitrant materials from the wastewater. Thus, it is of special interest to examine the sorbents developed in this study to combine with biological treatment.

## 1.2 Research Objectives

The goal of this research is to examine the low cost zeolite, e.g. rice husk ash-synthesized zeolite Y and natural mordenite, and their modified forms towards the removal of various contaminants in water including cation, inorganic oxyanions and anionic organic. Finally, small round shape particles were fabricated from the sorbents and applied together with microbial species to perform cleaning in wastewater treatment. The specific objectives of this research are:

- To synthesize zeolite Y by using rice husk ash as the silica source.
- To characterize the prepared zeolite Y and natural mordenite by a variety of method.
- To prepare surfactant-modified zeolites at different cationic surfactant loading.
- To examine the efficiency of the raw zeolites and modified zeolites for the removal of various contaminants of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$  and Acid Orange 7 in terms of kinetics and equilibrium studies.
- To isolate and screen the suitable bacteria from wastewater for contaminant removal.
- To fabricate zeolite particle (raw and modified forms) and use together with microbial community for wastewater treatment.

## 1.3 Scope and Outline of Thesis

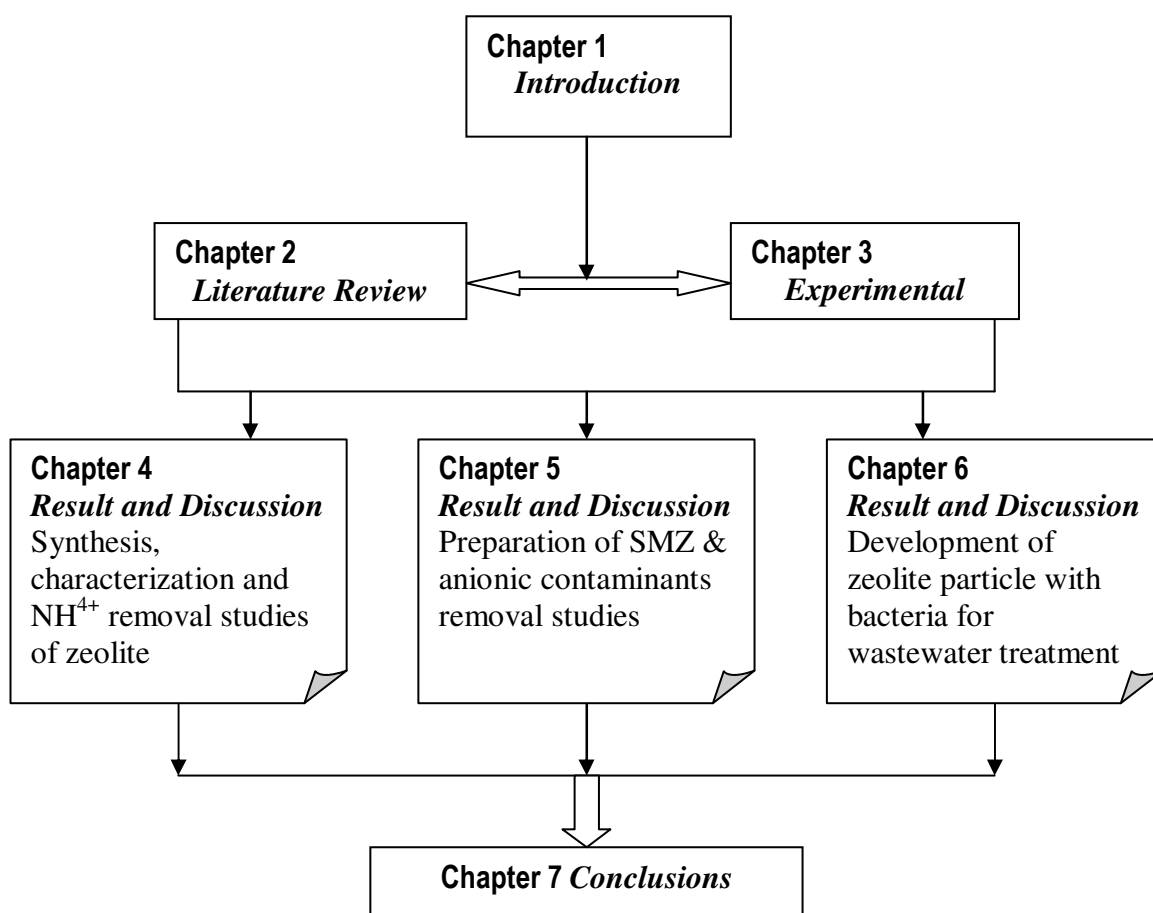
This thesis consists of seven chapters. Chapter 1 presents the general research background and scope of the work. Chapter 2 presents extensive review of research relevant to the present study. The third chapter describes the materials and the experimental details employed in this study, while Chapters 4 to 6 are results and discussions, it can be viewed as an independent study of each chapter, while in a broader sense, the three chapters together provide an overall picture of this research with significant relevancy. Finally, the concluding remarks can be found in Chapter

7. The outline of the thesis is discussed in more detail below. The relations between the various chapters are visualized in Figure 1.2.

- In Chapter 1, the general research background, research objectives, scope and outlines of thesis were presented.
- In Chapter 2, background knowledge and extensive review were provided in relevant to the present study. Basic background of zeolite was discussed in terms of physical features, framework topology, relationship of natural zeolite and synthetic zeolite. Then, hydrothermal synthesis of zeolite was discussed which include the general aspects, rice husk ash as an alternative silica source and in particular the methods of preparing synthetic zeolite Y. Extensive reviews were made on the previous developments of surfactant modified zeolites covering the fundamental aspects of surfactant and zeolite relationship, adsorption mechanism of SMZ, and previous applications of SMZ. Finally the synergistic advantages on the combination of adsorption and biological treatment are briefly reviewed.
- In Chapter 3, materials consumed, instruments applied and detailed experimental procedures in this study are described. The experiments consist of the preparation of zeolite and its modified form, characterization methods of materials, adsorption kinetics and equilibrium studies in batch mode, isolation and screening of pure colony of bacteria, zeolite particle preparation, the use of zeolite particle in wastewater treatment in combination with bacterial degradation.
- In Chapter 4, results and discussion on synthesis, characterization and ammonium removal studies of zeolite are presented. It includes characterization of RHA, synthesis of zeolite from RHA, characterization of zeolite by XRD, FT-IR, FESEM, EDAX, nitrogen adsorption studies, ammonium removal studies in which suitable kinetics and isotherms models were employed to investigate the adsorption behavior.
- In Chapter 5, results and discussion on the preparation of surfactant-modified zeolite and anionic contaminants removal studies are deliberated. Anionic contaminants investigated are nitrate, phosphate, sulfate and acid dye (Acid Orange 7). Pseudo second order kinetic was found fit to the adsorption kinetics

of SMZ towards anionic contaminants. Langmuir and Freundlich isotherms are employed to obtain the important adsorption parameters.

- In Chapter 6, results and discussion on the development of zeolite particle for wastewater treatment are presented. This chapter covers the performance of several types of bacteria to remove different contaminants, optimization and preparation of zeolite particle, and finally the use of zeolite particle (raw zeolite and SMZ) in textile wastewater treatment in coupling with mixed cultures of bacteria.
- In Chapter 7, the concluding remarks and some recommendations for further research can be found.



**Figure 1.2:** Outline of the thesis