DIRECT AND INDIRECT AQUEOUS MINERALIZATION USING RED GYPSUM FOR CARBON DIOXIDE SEQUESTRATION

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“To my beloved family”
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ABSTRACT

Carbon capture and storage is gaining prominence as a means of combating climate change. Mineral carbonation is the only known form of permanent and leakage-free carbon storage. The aim of this research was to investigate the suitability and feasibility of utilizing red gypsum as the calcium source for the mineral carbonation process. The physico-chemical analysis of red gypsum showed that calcium and iron are its major constituents, which makes it a highly suitable and potential feedstock for mineral carbonation. The direct carbonation of red gypsum showed that both the purity of the product and the efficiency of the reaction were very low even at elevated reaction temperature and CO₂ pressure. The maximum CaCO₃ purity of 23.63% and carbonation efficiency of 41.04% were achieved during direct aqueous carbonation of red gypsum. The red gypsum dissolution studies showed that H₂SO₄ resulted in higher calcium extraction efficiency compared to HCl and HNO₃. Increasing the reaction temperature from 30 °C to 70 °C and also increasing the reaction time from 5 to 120 minutes were found to be effective in enhancing the degree of extraction for all three types of acid used. The maximum of 100% and 84.6% extraction efficiency was achieved for Ca and Fe, respectively. Kinetic analysis found that the dissolution rate of red gypsum is controlled by the combination of product layer diffusion and chemical reaction control. The carbonation efficiency was found to be in direct relationship with CO₂ pressure where the maximum carbonation efficiency of 100% was achieved at 8 bar CO₂ pressure. The pH swing experiments resulted in CaCO₃ with a maximum purity of 98%. The pH swing carbonation of red gypsum could be further investigated as a promising method for large scale CO₂ sequestration.
ABSTRAK

Pemerangkapan dan penyimpanan karbon semakin terkenal sebagai satu cara untuk mengatasi masalah perubahan iklim. Pengkarbonan mineral adalah satu-satunya cara yang diketahui sebagai kaedah penyimpanan karbon secara kekal dan bebas daripada kebocoran. Kajian yang dijalankan ini adalah bertujuan untuk mengkaji kesesuaian dan kebolehlanjutan penggunaan gipsum merah sebagai sumber kalsium untuk proses pengkarbonan mineral. Analisis fiziko-kimia ke atas gipsum merah menunjukkan bahawa kalsium dan ferum adalah zat utamanya, yang menjadikan ianya sangat sesuai dan berpotensi sebagai sumber bahan mentah bagi proses pengkarbonan mineral. Proses pengkarbonan langsung ke atas gipsum merah menunjukkan hasil tindakbalasnya adalah sangat rendah terutama darisegi ketulenan produk dan kecekapan pengkarbonan langsung pada gipsum merah, didapati ketulenan maksimum sebanyak 23.63% manakala kecekapan pengkarbonan adalah sebanyak 41.04%. Kajian kebolehlarutan gipsum merah menunjukkan bahawa H₂SO₄ menghasilkan kecekapan pengkarbonan maksimum sebanyak 100% yang kalah 84.6%. Analisis kinetik mendapati bahawa kadar kebolehlarutan gipsum merah dipengaruhi oleh gabungan dua faktor iaitu serapan lapisan hasil bahan dan kawalan tindak balas kimia. Kecekapan pengkarbonan didapati mempunyai hubungan secara langsung dengan tekanan CO₂, yang mana kecekapan pengkarbonan maksimum 100% dicapai pada tekanan CO₂ 8 bar. Eksperimen pH-berubah dapat menghasilkan sebatian CaCO₃ dengan ketulenan maksimum sebanyak 98%. Dengan ini didapati bahawa pengkarbonan pH-berubah ke atas gipsum merah boleh dikaji selanjutnya kerana ianya amat berpotensi sebagai satu kaedah untuk proses pemencilan- CO₂ yang berskala besar.
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LIST OF SYMBOLS

GHG - Greenhouse gas
CO₂ - Carbon Dioxide
ppm - parts per million
IPCC - Intergovernmental Panel on Climate Change
Gt - Gigatone
°C - Degree Celsius
CCS - Carbon capture and storage
Ca - Calcium
Mg - Magnesium
Fe - Iron
Mg₂SiO₄ - Olivine
CaSiO₃ - Wollastonite
Mg₃Si₂O₅(OH)₄ - Serpentine
RG - Red gypsum
FeTiO₃ - Ilmenite
TiO₂ - Titanium dioxide
TiOSO₄ - Titanyl sulphate
FeSO₄ - Iron sulphate
CaSO₄.2H₂O - Gypsum
ppmv - parts per million per volume
TGA - Thermogravimetric analysis
DTA - Differential thermal analysis
FESEM - Field emission scanning electron microscopy
ICP-OES - Inductively coupled plasma optical emission spectrometry
FT-IR - Fourier transform infra-red spectroscopy
SEM - Scanning electron microscopy
XRD - X-ray diffraction
XRF - X-ray fluorescence
NaOH - Sodium hydroxide
KOH - Potassium hydroxide
NH₄OH - Ammonium hydroxide
H₂SO₄ - Sulphuric acid
HCl - Hydrochloric acid
HNO₃ - Nitric acid
rpm - Round per minute
mL - Millilitre
ln - Natural log
Ea - Activation energy
K₀ - Frequency factors
M - Molar
HPHT - High pressure high temperature
IEA - International Energy Agency
C - Carbon
ppb - parts per billion
Mg₂SiO₄ - Forsterite
Fe₂SiO₄ - Fayalite
Mg₃Si₄O₁₀(OH)₂ - Tale
CaMgSiO₆ - Diopside
SiO₂ - Quartz
Fe₂Mg₅(SiO₄)₂ - Kondrodite
H₄Ca₁₂Al₆Si₁₀O₄₃ - Vesuvianite
CaMg₂Si₄O₁₂ - Tremolite
BF - Blast furnace
LF slag - Ladle furnace slags
EAF - Electric arc furnace
BOF - Basic oxygen furnace
CKD - Cement kiln dust
MSW - Municipal solid waste ash
BA - Bottom ash
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<td>APC</td>
<td>Air pollution control</td>
</tr>
<tr>
<td>µm</td>
<td>Micron meter</td>
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<td>MgCO₃</td>
<td>Magnesium carbonate</td>
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<td>CaCO₃</td>
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<tr>
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<td>Mega Pascal</td>
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<tr>
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</tr>
<tr>
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<td>Ammonium chloride</td>
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<tr>
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<td>Ground granulated blast furnace slag</td>
</tr>
<tr>
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<td>Phosphorus slag</td>
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<tr>
<td>SS</td>
<td>Steel slag</td>
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<tr>
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<tr>
<td>g/L</td>
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<tr>
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<tr>
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<tr>
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<tr>
<td>Symbol</td>
<td>Definition</td>
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<tr>
<td>$\text{FeSO}_4$</td>
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CHAPTER 1

INTRODUCTION

1.1 Introduction

It is postulated that the current warming of the global climate is the result of the increase in anthropogenic greenhouse gas (GHG) emissions, particularly carbon dioxide (CO₂) since the beginning of the industrial revolution (IPCC, 2007). The average atmospheric CO₂ has increased from 280 ppm in the 1750s to 389 ppm in 2010 (IPCC, 2005; IPCC, 2007; Bobicki et al., 2012). The increase in atmospheric CO₂ over the last two and a half centuries has been attributed to two major anthropogenic forcing fluxes: (i) emissions from fossil fuel combustion and industrial processes and (ii) land use change (Canadell et al., 2007; IPCC, 2007; Raupach et al., 2007). Because the use and supply of global energy is projected to grow, especially as developing countries pursue industrialization, fossil fuels are expected to maintain their dominance in the global energy mix until 2030 and beyond. If no proactive mitigative action is taken, energy-related CO₂ emissions are likely to be 40-110% higher in 2030 than they were in 2000 (23.5 Gt CO₂ per annum) (IPCC, 2007; IEA, 2011). The latest figures indicate that the world CO₂ emission from fuel combustion was 29.4 Gt in 2008 (IEA, 2011). By 2100, atmospheric CO₂ concentrations could reach 540-970 ppm (IPCC, 2001), resulting in a global mean temperature increase of 1.8–4 °C (IPCC, 2005). It is recognized that a temperature increase of this magnitude would have wide-ranging and drastic implications for water and food availability, human health, ecosystems, coastlines and biodiversity (Kiehl and Trenberth, 1997; Yamasa-
Reducing the energy intensity, switching to non–fossil fuels, and enhancing CO$_2$ sequestration by developing technologies to capture and sequester more CO$_2$ are the available and applicable methods of reducing the CO$_2$ concentration. However, in a short-to-medium period, CO$_2$ sequestration methods are necessary to implement to avoid further increase of CO$_2$ (Raupach et al., 2007; Bobicki et al., 2012). The contribution of up to 15–55% of the cumulative global climate change mitigation effort by 2100 has been predicted by carbon capture and storage (CCS) methods. Moreover, improvements of CO$_2$ sequestration methods, the increase of their effectiveness and the change to a carbon-free fuel, such as renewables, are very important to achieve a sustainable energy system (Yamasaki, 2003; IPCC, 2005).

The basic steps of CCS methods consist of post–combustion and pre–combustion CO$_2$ capture, separation from other gases, transportation to the sites, and CO$_2$ isolation from the atmosphere via storage. CO$_2$ sequestration is a process that involves all four steps of CO$_2$ capture, separation, transportation, and finally storage. Geological CO$_2$ storage, ocean storage, below seabed storage, and CO$_2$ mineral sequestration are the practical techniques of CO$_2$ sequestration (Svensson et al., 2004; Gibbins and Chalmers, 2008; Olajire, 2010).

Geological storage is the injection of CO$_2$ into abandoned underground gas/oil fields or saline formations to improve the oil, gas, and coal bed methane recovery from reservoirs. Several projects operating in Norway (such as the Sleipner project), Canada, Algeria, Australia, and other locations are examples of the use of this method throughout the world. However, the lack of permanency, the risk of leakage and the post–monitoring of the site are the problems and challenges associated with this method (IPCC, 2005). CO$_2$ injection into the great depth of ocean water results in carbonate production due to the reaction of CO$_2$ with ocean water and carbonic acid dissociation. Ocean storage is very suitable for CO$_2$ reduction; however, environmental issues, such as decreasing of water pH and the lack of permanency,
have made this method unattractive in recent years (Huesemann, 2006; Bobicki et al., 2012). CO₂ storage below the ocean floor at depths of at least 3,000 m of ocean and several hundred meters of marine sediment is called below seabed storage. The lack of permanency and post–monitoring of the site (negative points of geological and ocean storage) do not exist with below seabed storage method; however, this method is still new and requires further research (House et al., 2006).

Mineral carbon dioxide sequestration is an exothermic chemical reaction of a metal–bearing oxide, usually calcium (Ca), magnesium (Mg), or iron (Fe), with CO₂ to form stable solid carbonates. Carbonation can take place either in-situ or ex-situ (Bobicki et al., 2012). In–situ carbonation is the reaction of CO₂ with Mg and Ca minerals underground where CO₂ is being injected, and ex-situ carbonation is the same reaction taking place above ground in a chemical processing plant (Lackner et al., 1995; Gerdemann et al., 2004). The CO₂ mineralization, or mineral carbonation, is an artificial rock weathering and was first proposed by Seifritz in 1990, whereas natural rock weathering is a geological time-scale process (Seifritz, 1990). Mineral carbonation provides a permanent and leakage–free CO₂ disposal method in that the produced carbonates are environmentally benign and stable (Maroto–Valer et al., 2005). The produced carbonates are also profitable because Ca and Mg carbonates are widely used industrially, such as in papers, paints, plastics, adhesives, sealants, cosmetics, flooring, fireproofing and fire–extinguishing industries (Bobicki et al., 2012).

Alkaline earth metals, such as Ca and Mg, are the most favorable metals for mineral carbonation (Huijgen and Comans, 2003). However, these minerals are usually rare in nature due to their high reactivity, and they usually appear in the form of silicates. The most common natural silicate minerals are olivine (Mg₂SiO₄), wollastonite (CaSiO₃), and serpentine (Mg₃Si₂O₅(OH)₄) (Lackner et al., 1995; Huijgen and Comans, 2003). In addition to the natural minerals, industrial solid residues and wastes rich in Mg and Ca are also potential materials to be used as carbonation feedstocks. Some more investigated and well–known waste solids, such as waste ashes, waste cement, steelmaking slag, and mining wastes, can also be used as carbonation

Red gypsum (RG) is a by-product produced during titanium dioxide (TiO$_2$) production from ilmenite (FeTiO$_3$) ores. Ilmenite contains approximately 43-65% titanium dioxide and is widely used as raw material for titanium dioxide manufacturing. Titanium dioxide is extracted from ilmenite through stepwise processes. The first step is the chemical reaction of ilmenite with sulfuric acid to digest the ore. In this step, the titanyl sulfate (TiOSO$_4$) and iron sulfate (FeSO$_4$) are produced. The second step is the clarification of produced liquor through solid separation. This is followed by the hydrolyzation of the liquor by steam for TiO$_2$ precipitation. Finally, the hydrated TiO$_2$ is separated and washed with water to remove the impurities. The neutralization of the spent sulfuric acid during TiO$_2$ extraction with limestone and lime produces a by-product named RG (CaSO$_4$.2H$_2$O). In the next step, the RG is filtered and separated from water, and the produced water is recycled in the process. This waste product is disposed of in landfill areas or left as stacks close to the titanium dioxide industry. RG is rich in Ca and Fe (more than 70%), which makes it a very potential feedstock for mineral carbonation. The titanium dioxide industry in Malaysia produces 400,000 tons of RG annually that could be utilized for CO$_2$ sequestration (Fauziah *et al.*, 1996, Azdarpour *et al.*, 2014).

### 1.2 Problem Statement

One main technical parameter makes the mineral carbonation process industrially viable. The process must result in high carbonation efficiency and products purity at low operating conditions, which means at low CO$_2$ pressure and reaction temperature (Bobicki *et al.*, 2012). The main barriers to the commercial deployment of mineral carbonation are low carbonation conversion and slow reaction kinetics. It has been stated in the literature that carbonation through direct mineral carbonation results in low carbonation efficiency and product purity. This is because the process suffers from thermodynamic limitations, which results in low overall carbonation
efficiency (O’Connor et al., 2000a; O’Connor et al., 2000b; Gerdemann et al., 2004). In some of the studies in the literature, moderately high carbonation efficiencies have been reported; however, critical analysis of those studies reveals that relatively high CO\textsubscript{2} pressure and reaction temperature have been utilized. This inherently increases the overall cost and required energy of the project and prevents the project from being implemented in large-scale (Lackner et al., 1997; Fauth et al., 2000; Fauth et al., 2002; Goldberg and Walters, 2002). In some of the studies in the literature, even at relatively high CO\textsubscript{2} pressure and reaction temperature, the overall carbonation efficiency is still low, which hinders the process from being implemented in large-scale (Béarat et al., 2002; Huijgen et al., 2006; Lammers et al., 2011). Another problem arises from mining and pretreatment of feedstocks. The natural minerals require mining activities, energy-intensive pre-treatments, such as fine grinding, heat treatment, and chemical activation with strong acids, to provide adequate conversions and reaction kinetics. These activities increase the overall required energy of the carbonation process (Lackner et al., 1997; O’Connor et al., 2001; Goldberg et al., 2002; Huijgen et al., 2006; Teir et al., 2005; Teir et al., 2007a; Teir et al., 2007b).

Therefore, carbonation through an indirect process has been proposed in this study to improve the carbonation efficiency and product purity. In addition, this research is aimed to utilize the by-product red gypsum, an industrial waste rich in Ca and Fe, as a feedstock for the mineral carbonation process.

1.3 Research Objectives

This research investigated the suitability and feasibility of utilizing RG as the Ca source for mineral carbonation processes. In addition, this research also investigates the effects of different reaction conditions, such as temperature, CO\textsubscript{2} pressure and particle size, on the overall carbonation process in a wide range, not only at certain limited values. Based on the research novelty and also the contributions to the literature, the objectives of this research are defined as follows:
1. To determine physico-chemical properties of red gypsum as the feedstock

2. To evaluate the feasibility of the red gypsum for carbonation through direct carbonation

3. To evaluate the efficiency of calcium and iron extraction from red gypsum by using different acids and bases along with kinetic analysis for indirect carbonation process

4. To determine the effect of CO$_2$ pressure on the overall carbonation of pH swing process

1.4 Research Scope

In this research, RG (CaSO$_4$2H$_2$O), a by-product from the titanium dioxide industry that is rich in Ca and Fe, is selected as the potential feedstock for mineral carbonation purposes. This research consists of four main steps, including characterization of raw red gypsum in the first step, direct carbonation of RG in the second step, Ca extraction from RG in the third step and, finally, implementation of the pH swing process at different CO$_2$ pressures. These four main steps are designed and aimed in such a way to cover all objectives of this study.

RG is characterized physically, chemically, and mineralogically using inductively coupled plasma optical emission spectrometry (ICP-OES), flourier transform infrared (FT-IR) spectroscopy, X-ray fluorescence (XRF) analysis, thermogravimetric analysis (TGA), field emission scanning electron microscopy (FESEM), particle size distribution (MASTERSIZER 2000) analysis, and X-ray diffraction (XRD) analysis.
For the direct carbonation of RG, different CO$_2$ pressure of 1 to 70 bar in conjunction with different reaction temperature of 25 to 300 °C applied. In addition, RG with several range of particle size of less than 45 microns, 45-75, 75-100, 100-212, 212-300, 300-400, and 400-500 microns utilized. In these experiments, NH$_4$OH used as a basic solution in all experiments. All carbonation experiments conducted in a 100 mL autoclave mini reactor capable of withstanding a maximum pressure of 200 bar and maximum temperature of 450 °C.

In the third step of this research, H$_2$SO$_4$, HCl and HNO$_3$ with variable concentrations of 0.1 to 4 M utilized to extract Ca from RG. A stirring rate of 1000 rpm used consistently in all experiments. The reaction temperatures of 25, 30, 50 and 70 °C in conjunction with variable reaction times of 5 to 120 min utilized. All dissolution experiments carried out in a 500 mL spherical glass batch reactor. In addition, the kinetic analyses performed using heterogeneous reaction models and pseudo-homogeneous models. Finally, Arrhenius plot used to calculate the activation energies (Ea).

In the final step, initially 2 M H$_2$SO$_4$ was used for RG dissolution at 70 °C with 60 min reaction time and 1000 rpm stirring rate. NH$_4$OH was used to remove impurities from the Ca-rich solution. The carbonation experiments performed under CO$_2$ initial pressure of 1 to 70 bar at a constant reaction temperature of 25 °C. A 100 mL autoclave mini reactor with temperature controller was used for all carbonation experiments.

1.5 Significance of the Study

Increasing anthropogenic greenhouse gas emissions and, in particular, CO$_2$ have caused the current warming of the global climate (Canadell et al., 2007; IPCC, 2007). Excessive fossil fuel combustion, industrial processes and land use changes are considered as the main causes of increasing the atmospheric CO$_2$ concentration.
(IPCC, 2007; Raupach et al., 2007). In this regard, stabilization of the atmospheric CO$_2$ concentration is of great importance (Bobicki et al., 2012). CCS involves separation of CO$_2$ from gaseous wastes, transportation to storage sites and, finally, long term isolation from the atmosphere. CCS has been proposed as a bridging technology that will allow CO$_2$ emissions to be managed during fossil fuel dependence while the effort for the use of renewable energy sources steadily increases (van Alphen et al., 2010a, van Alphen et al., 2010b). Mineral carbon sequestration of RG is one of the CCS technologies that provide a safe and leakage-free CO$_2$ isolation. This study is aimed to discover implementations that will reduce the atmospheric CO$_2$ concentration. This is because RG contains significant amounts of Ca and Fe (more than 33%), which makes it a very potential feedstock for mineral carbon sequestration processes. Therefore, mineral carbonation of RG will be able to play a significant role in reducing the concentration of CO$_2$ in the atmosphere. The objectives of this study are designed in such a way that the findings can contribute to the literature data significantly.

This study presents various major contributions to the literature. This research provides comprehensive details regarding the physical and chemical properties of RG. The findings of RG’s characterization can be used as a reference for future works. This study also provides knowledge to determine the most effective acid for maximizing the extraction rate of Ca from RG. In addition, the kinetics involved during Ca extraction from RG are introduced. Moreover, this study provides comprehensive knowledge regarding the feasibility of direct and indirect carbonation of RG. The carbonation efficiency and CaCO$_3$ purity are investigated in direct and indirect carbonation under different operating conditions. These findings can be used as valuable references for designing the most effective and feasible carbonation method with the aim of maximum conversion rate with minimum energy loss.

Another significance of this study is the possibility of waste management. RG is considered a waste of titanium extraction industries that is usually accumulated in landfills. Malaysia is considered one of the major RG producers in the world. Therefore, utilization of this waste as a potential feedstock for mineral carbonation processes, alongside process optimizations for large-scale implementation could be a
significant achievement in CO$_2$ mitigation strategies. In addition, the produced carbonates have some industrial applications, such as in papers, paints, plastics, adhesives, sealants, cosmetics, flooring, fireproofing and fire-extinguishing industries (Eloneva et al., 2008; Eloneva et al., 2010, Bobicki et al., 2012).

1.6 Organization of the Thesis

This thesis is organized into six chapters. A brief outline of the contents of the thesis is as follows:

**Chapter 1** presents an introduction to the research problem. It involves the background and significance of the research, as well as the problem statement and contributions.

**Chapter 2** is devoted to the literature study that has been carried out in relation to subjects concerning this thesis. Firstly, energy dependency on fossil fuels and, consequently, GHG emissions and the global warming phenomenon are studied. Secondly, CCS as one of the key elements in CO$_2$ mitigating scenarios is reviewed and discussed. Finally, mineral carbonation as the main focus of this research is critically described and reviewed. Suitable feedstocks, carbonation routes and parameters affecting the overall process are critically addressed.

**Chapter 3** focuses on introducing methodologies to achieve the designed objectives of this research. Methodologies to conduct RG characterization, direct carbonation of RG, Ca/Fe extraction from RG, and pH swing carbonation of RG are fully designed and described in this chapter.

**Chapter 4** presents the results of RG characterization as well as direct carbonation of RG. The characterization studies include physical and chemical analysis of RG. The results of direct carbonation of RG are expressed in terms of product pu-
rity and carbonation efficiency with respect to variable RG particle size, different CO₂ pressure and reaction temperature.

**Chapter 5** presents the results of RG dissolution and pH swing carbonation. In the first section, the dissolution results are presented in terms of Ca/Fe extraction efficiency with respect to different reaction temperatures and times. In addition, kinetic analysis results are also provided to support the experimental findings. In the second section, the results of the pH swing carbonation experiments with different CO₂ pressures are provided. The results are expressed in terms of product purity, carbonation efficiency and removal efficiency.

**Chapter 6** sums up the research findings and outlines the directions for future research works.
REFERENCES


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