Catalytic performances of clay-based materials in hydride formation

by

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Dissertation submitted in partial fulfillment

of the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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Approved by,

(Dr. BAWADI B ABDULLAH)

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

CHARIYEV BAYRAM

ABSTRACT

Nowadays, hydrogen is considered to be one of the best alternatives for the replacement of the gas and oil product fuels. In spite of that, using of hydrogen as a fuel brings a problem with a storage as hydrogen is very volatile and occupies a lot of volume. Hydrogen storage in the metal hydride form will eliminate the usage of bulky and heavy cylinders required for storing hydrogen gas in a compressed form and expensive vessels to store liquid hydrogen. When storing hydrogen in the form of metal hydrides by intercalating H_2 atoms into the metals, the volume of the system decreases by about 3 times as compared with the volume of storage in cylinders. The adsorption and desorption process of hydrogen molecules into the metals can be initiated by using of hydrotalcite $Mg_6Al_2CO_3(OH)_{16}\cdot 4(H_2O)$, also known by the name of aluminum–magnesium layered double hydroxide or anionic clay. The mixed oxides of hydrotalcite have gained enormous attention that was designed as adsorbent and can be a potential hydrogen storage material because of its physisorption capacity of hydrogen in a molecular form. In this project, the study aims to develop lithium based hydrotalcite derived mixed oxides and to convert their hydrides to store large amount of hydrogen.

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ABBREVIATIONS AND NOMENCLATURES

Mode	**Abbreviation**	**Full name**
Chemicals	H_2	Hydrogen gas
	$Al(NO_3)_3 \cdot 9H_2O$	Aluminum nitrate nonahydrate
	$Mg(NO_3)_2 \cdot 6H_2O$	Magnesium nitrate hexahydrate
	$Ni(NO_3)_2 \cdot 6H_2O$	Nickel nitrate hexahydrate
	$Na_2CO_3 \cdot 10H_2O$	Sodium carbonate decahydrate
	$LiNO_3$	Lithium nitrate
Equipment	FESEM	Field Emission Scanning Electron Microscope
	RAMAN	Raman Spectroscope
	XRD	X-ray Diffractometer

CHAPTER 1

INTRODUCTION

1.1 Project Background

Hydrogen is the best candidate as an energy source for mobile and stationary applications. Unlike petroleum products, hydrogen can be easily produced from renewable energy sources. It is also an environmental friendly source of energy by forming the water as a clean byproduct during the usage. Yet it is a problem to store the hydrogen that makes its usage too limited as a fuel. Hydrogen storage is certainly one of the important challenges for development of the hydrogen economy. One gram of hydrogen gas occupies approximately 11 liter of space in normal conditions at atmospheric pressure, so for simplicity the gas must be highly pressurized to several hundred atmospheres and stored in a pressurized vessel. So far hydrogen can be stored as (1) compressed gas, (2) a cryogenic liquid, (3) as a solid fuel in a chemical or physical combination with metals. The common ways of hydrogen storage by using compressed gas and cryogenic liquid facilities are complicated due to low boiling point ($-252.87\ \mathrm{C}^{\circ}$) and low density of hydrogen in the gaseous form (0.08988 g/L) at 1 atm. Hydrogen can be stored in the liquid form only at cryogenic temperatures. These options are not applicable for everyday requirements.

The solution to these obstacles is the storage of hydrogen in the metal hydride form. This method uses the metal that can absorb and keep the big amounts of hydrogen by combining with hydrogen and forming metal hydrides. The hydrogen storage in the metal hydride form is capable of absorbing and releasing hydrogen without damaging its own structure. Hydrogen can form metal hydrides with some certain metals and alloys which leads to solid-state storage of the gas under normal temperature and pressure that provides them with an important safety advantages rather than gas and liquid storage methods. Hydrogen-storage capacity of metal hydrides are higher with the density of (6.5 H atoms/cm^3 for MgH_2) compared to hydrogen gas (0.99 H atoms/cm^3) and liquid hydrogen (4.2 H atoms/cm^3). And also storing hydrogen in metal hydride form is a safe and volume-efficient storage technique for on-board vehicles. Maximum hydrogen storing material must have this following properties; high hydrogen content per unit mass and unit volume, low dissociation temperature and moderate dissociation pressure, low heat of formation to minimize the energy required for hydrogen release, low heat dispersion during the exothermic hydride formation, reversibility, high kinetics, high stability against O2 and moisture for its life cycle with high level of safety.

Lithium based hydrotalcite derived mixed oxides will be studied due to its high gravimetric and volumetric hydrogen storage density. Also this metal is highly available in the market. Form the literature it is known that magnesium can form the structure of magnesium hydride with 7.6 weight percentage of hydrogen content. Nickel source was used as a catalyst to dissociate hydrogen and increase the hydrogen sorption process. The combination of hydrogen with magnesium forms the intermetallic compound of alkali hydride. This metal is a promising candidate for hydrogen storage because of its capability to store hydrogen at near ambient conditions by physical or chemical way. Also this metal possesses favorable hydrogen release thermodynamics and kinetics at low decomposition temperature.

1.2 Problem Statement

Hydrogen fuel is considered to be one of the best alternative energy sources among the others for the future requirements. With the usage of hydrogen as a fuel, it needs to be stored in a tanks and vessels in the form of compressed gas or cryogenic liquid which is a very expensive and unsafe method. None of the mentioned technologies fulfill the criteria for efficient hydrogen storage. A lot of researches have been directed for the development of light-weight high amount hydrogen containing chemical for on-board hydrogen storage applications. Storing the hydrogen in the form of metal hydrides is considered to be best the way which satisfies the criteria for effective hydrogen storage method. Many researches are aimed to find out the best metals that can easily adsorb and desorb hydrogen atoms and also develop hydrogen adsorbing materials or clays which can capture hydrogen and intercalate them into metals to obtain metal hydrides. So in this study, the research focuses on clay based materials synthesis with the combination of different metals for capturing higher content of hydrogen.

1.3 Objectives

The objectives of this project are:

i. To prepare/derive highly hydrogen concentrated metal hydride from clay based materials.
ii. To evaluate the performances of adsorbents for their adsorption and desorption capacity.
iii. To characterize the synthesized adsorbent by using XRD, FESEM and RAMAN.

1.4 Scope of Study

In the final year project, it is expected to derive highly hydrogen concentrated metal hydride by using clay based material as an adsorbent. The physio-chemical characteristics and morphologies of adsorbents will be investigated by using X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) and RAMAN spectroscopy.

The performance of the clay based material will be investigated by conducting a laboratory scale experiment for hydrogen adsorption and desorption capability.

CHAPTER 2

Literature Review

2.1 Metal hydrides

Hydrides are divided into three types: metallic, ionic and covalent.

Ionic hydrides - usually generated at high pressures (~ 100 atm.) And at temperatures greater than 100°C. Typical example for ionic hydrides is an alkali metal hydrides. Outstanding feature of ionic hydrides is that it contains higher density of atoms rather than in its initial form.

Covalent hydrides - hardly find applications because of the low stability and high toxicity of metals and intermetallic compounds. A typical example is a beryllium hydride, obtained by the reaction of lithium aluminum hydride with dimetilberillium in diethyl ether solution.

Metal hydrides - can be considered as alloys of metallic hydrogen, these compounds have high electric conductivity as their primary metals. Almost all transition metals can form metal hydrides. Depending on the type of bond, metal hydrides can be covalent (e.g. magnesium hydride) or ionic. Almost all metal hydrides require high temperatures for dehydrogenation to release hydrogen atom.

The best metal for hydrogen storage is palladium (Pd). In 1 % volume of palladium can be packed almost 850 % times more volume of hydrogen. But in spite of being such a good metal hydride for hydrogen storage palladium is very costly what makes this metal not usable for this purpose. In contrast, some metals such as copper (Cu) can dissolve only 0.6 % volumes of hydrogen per 1% volume of copper. The following is the metals that do not absorb hydrogen atom: Ag, Au, Cd, Pb, Sn, and Zn.

The present review shows latest developments of metal hydrides on properties including hydrogen-storage capacity, cyclic behavior, kinetics, toxicity, pressure and thermal response. The group of Mg-based hydrides seems as a promising candidate for the best hydrogen storing material with reversible hydrogen capacity up to 7.6 wt % for on-board applications. Many efforts have been dedicated to these materials in order to decrease their desorption temperature and enhance their kinetics and life cycle. The kinetics was improved by addition of a proper catalyst into the system and also by ball-milling technique that shows defects with improved surface properties. The studies brought desirable results, such as improved kinetics and lower decomposition temperatures, nevertheless materials are still far from fulfilling the planned target for their transport applications. Thus, further research work is required to reach the target by enhancing development on hydrogenation, thermal and cyclic behavior of metal hydrides. (Sakintuna, B., et al. 2007)

2.2 Synthesis of metal hydride

The synthesis of the alkali metal hydrides is an exothermic process (between 50 and 180 kJ/mol), however the direct synthesis by using reaction of hydrogen on the molten metal is a very slow process because of the protection taken by the hydride layer, formed instantly on the surface of the metal and which in turn slows the diffusion of the metal vapor and hydrogen. Rubidium and cesium hydrides are not available in the market and have to be synthesized at the laboratory scale. There are two ways, based on the reaction of hydrogen on the molten metal in the existence of a temperature gradient: the metal is heated up approximately at 250°C, where the temperature is high enough to partially decompose the hydride formed on its surface. The metal vapor is in equilibrium with hydrogen and the free metal distillates towards the cold part of the apparatus, whose temperature is 150°C. Near to the cold wall, it reacts with hydrogen and the formed hydride is collected on that cold area. At that temperature, the decomposition pressure of the hydride is insignificant which approximately 10^{-2} Torr is. The rate of the reaction is limited because of the low metal vapor pressure and the product is roughly 400 mg per day for 1 cm^2 of surface of the molten metal. The source of the hydrogen is either the flow of gas in an open circuit at atmospheric pressure, with probability of explosion or the gas coming from the thermal decomposition of uranium hydride heated at 450°C, with the problems connected to the radioactivity and toxicity of uranium. It is required to set up a new synthesis method for amounts higher than 1 g. (Elansari, L., et al. 2001)

The industrial synthesis of the alkali metal hydrides is based on the reaction of hydrogen on the molten metal dispersed in a mineral oil stirred, in order to renew the surface of the metal. The mechanical alloying is known for its continuous precise cleaning the surface of the reactants and then, constituting a chosen tool for such a synthesis. Mechanical alloying is also used for synthesis of several hydrides particularly with Mg, Ti, Zr .(Elansari, L., et al. 2001)

2.3 Limitations of metal hydride

In spite of its high capacity and instant low temperature kinetics, the metal hydrides at the meantime are not applicable storage system for many applications because they cannot be re-hydrogenated at acceptable pressures and temperatures. The main obstacle for the usage of metal hydrides as a form of hydrogen source in the mobile fuel cell appliances is the price related for the production of the material. Even though these materials can be easily synthesized by a variety of chemical processes, the price of the previous productions is usually intolerably high for mass production in the market. Because of this and also including environmental reasons, there is a lot of concern for identification of a closed loop regeneration process where all the materials excluding hydrogen are used again to reproduce the hydride. Sadly, the byproducts that appears in the process of the chemical synthesis in all hydrides are stable compounds like LiCl which are energetically expensive to separate and recycle. Latest study on AlH_3 showed that even under the best conditions, an ideally effective recycling reaction for AlH_3 might yet demand an energy uptake of 167 kJ/mol H_2, which is equal to about 70% of the fuel energy produced by AlH_3 . To be more realistic, it would require much more energy input to make this process in the industrial scale, much more energy than the energy stored within material. Taking into account the high costs related with the straight chemical synthesis, it is sensible to think of the alternative ways of reproducing the hydride from the spent material by depleting hydrogen. Because of its high instability, metal hydrides do not easily re-hydrogenate under moderate conditions of pressure and temperature. (Graetz, J. 2012)

2.4 Clay for synthesis of metal hydride

One of the ways of hydriding the metal is the adsorption of hydrogen in to the metal by using hydrotalcite $Mg_6Al_2CO_3(OH)_{16}\cdot 4(H_2O)$ or anionic clay. Hydrotalcite is a synthetic compounds with a structure based on the magnesium hydroxide-like layers where some of the divalent cations were replaced by trivalent cations. Hydrotalcite derived mixed oxides are particularly important in the formation of fine metal particles in the reduction. The surface of reduced mixed oxides is reactive which leads to the formation of possible outcomes. Hydrogen gas can undergo a chemical reaction with the primary side of the hydrotalcite derived metals oxides. Following the treatment of hydrogen where it undergoes reduction process, mixed oxides have anionic vacancies obtained by the removal of water. This vacancies formed on the surface of solid particles are able to capture hydrogen in the hydride form. (Salam, M. A., et al. 2013.)

The general formula for the hydrotalcite or layered double hydroxides (LDH) can be expressed as $[M^{z+}_{1-x}M^{3+}_{x}(OH)_2]^{q+}(X^{n-})_{q/n}\cdot yH_2O$, where water content of (y) can vary over a wide range. Most commonly, z = 2, divalent cations are $M^{2+} = Ca^{2+}$, Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} or Zn^{2+}; hence q = x. And with z = 1, where $M^+ = Li^+$ and trivalent cation $M^{3+} = Al^{3+}$. In this case, q = 2x - 1. LDHs can be formed with a different types of anions X (e.g. Cl^-, Br^-, NO_3^-, CO_3^{2-}, SO_4^{2-} and SeO_4^{2-}).

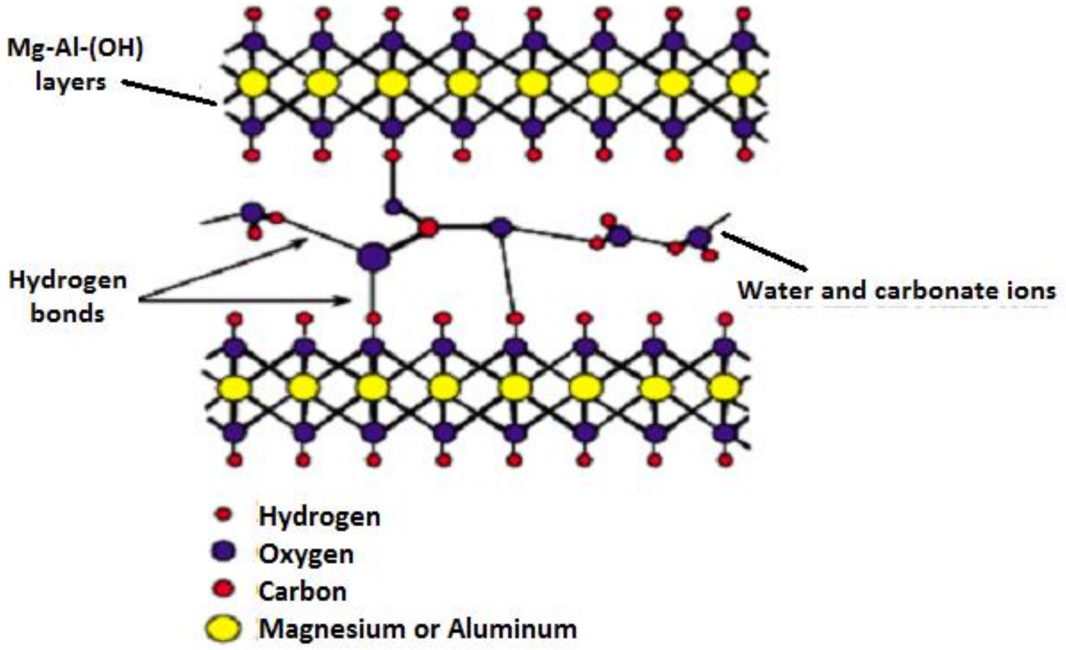


Figure 1: Hydrotalcite molecular structure

According to Salomão, R., et al. (2011), referring to the various types of hydrotalcite, the magnesium–aluminum one (MAH) has been deeply investigated over the past years. There were various ways to synthesize MAH, with different time-energy profiles, purity requirements for the reactants and for the final compound had been attained. The most common route was based on the co-precipitation process, which started with the preparation of an aqueous solution of magnesium and aluminum salts $MgCl_2$ and $AlNO_3$.

Chapter 3

Methodology

In this part of the report it is discussed about the research methodology and project activities that was planned for the accomplishment of this project. The methodology includes discussion on the process flow, the synthesis method of clay based material, the tools and equipment required, and chemicals that have been used for the experiment. All planned works were included in the Gantt chart and Key milestone.

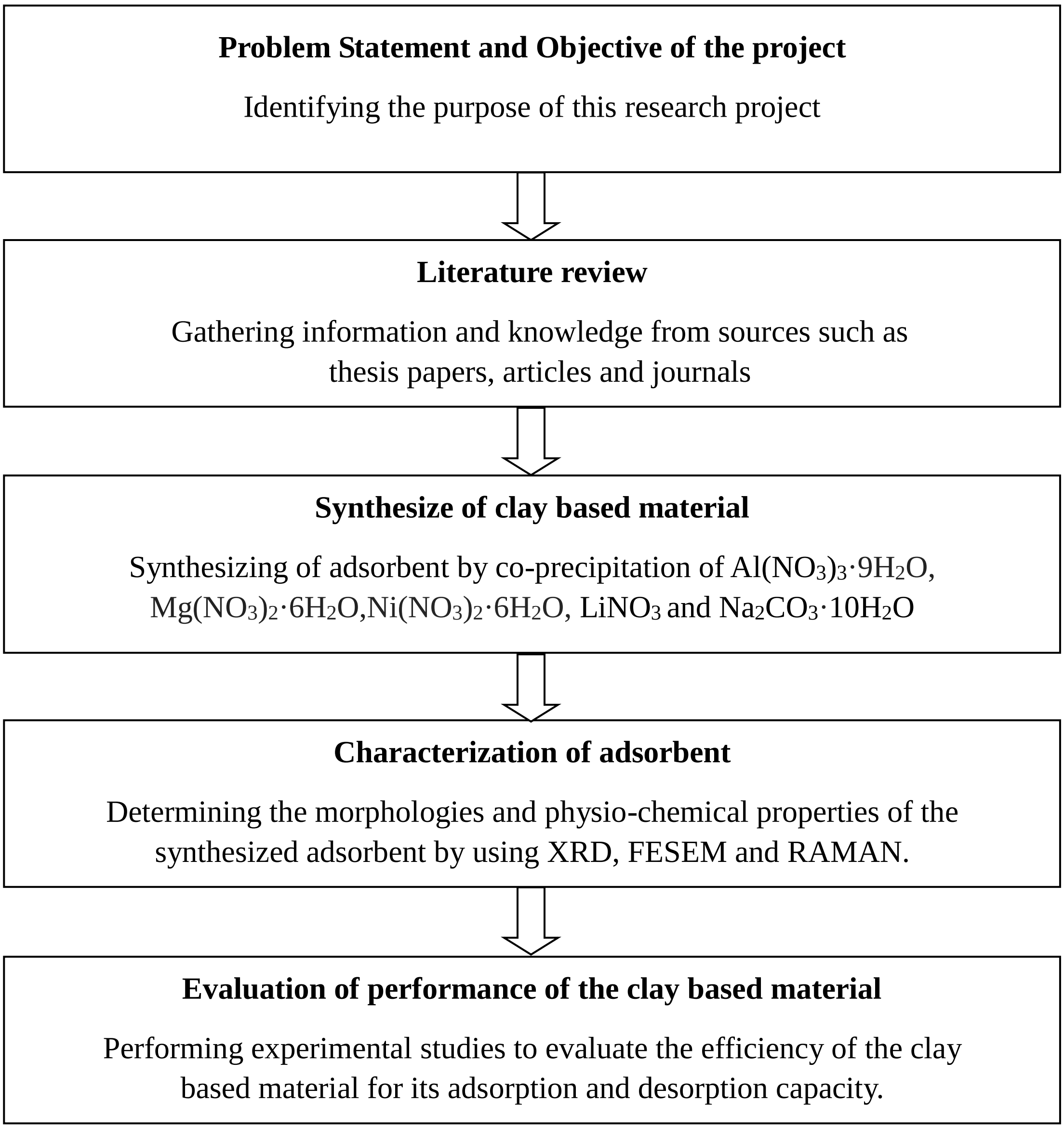
3.1 Research Methodology

The title has been assigned to student. This step is about focusing on statement analysis for the topic area and scope of the title. The title guided the direction of the project study. The information which is related to the project area has been searched and collected. The research was conducted starting with literature review on the synthesis of clay based material. Literature review has been done through analysis of related journals, thesis papers and all other useful references. It aimed to collect wider information about the research topic as well as updating the author on the current state of developments in the research area. By reviewing the literature and fully comprehending the idea behind it, the work on this project was initiated.

This project was based on the experiment and as soon as the literature review was completed, the experimental work has been conducted to synthesize the lithium based hydrotalcite derived mixed oxides to evaluate their efficiency of absorbing large amount of hydrogen. The physio-chemical characteristics and morphologies of the adsorbents were characterized by special equipment in the lab.

3.2 Process Flow

Figure below describes the sequence of work load performed in order to complete the project on time. The parts of the flow chart listed below were performed during Final Year Project 1 and 2 courses.



Problem Statement and Objective of the project

Identifying the purpose of this research project

Literature review

Gathering information and knowledge from sources such as thesis papers, articles and journals

Synthesize of clay based material

Synthesizing of adsorbent by co-precipitation of $Al(NO_3)_3{\cdot}9H_2O$, $Mg(NO_3)_2{\cdot}6H_2O$,$Ni(NO_3)_2{\cdot}6H_2O$, $LiNO_3$ and $Na_2CO_3{\cdot}10H_2O$

Characterization of adsorbent

Determining the morphologies and physio-chemical properties of the synthesized adsorbent by using XRD, FESEM and RAMAN.

Evaluation of performance of the clay based material

Performing experimental studies to evaluate the efficiency of the clay based material for its adsorption and desorption capacity.

Figure 2: The sequence of work

3.3 Synthesis of adsorbents by co-precipitation method

The lab work of the project started by synthesizing of the clay based material by co-precipitation method to produce hydrotalcite derived mixed oxides. Below is shown the steps for the synthesis of adsorbent.

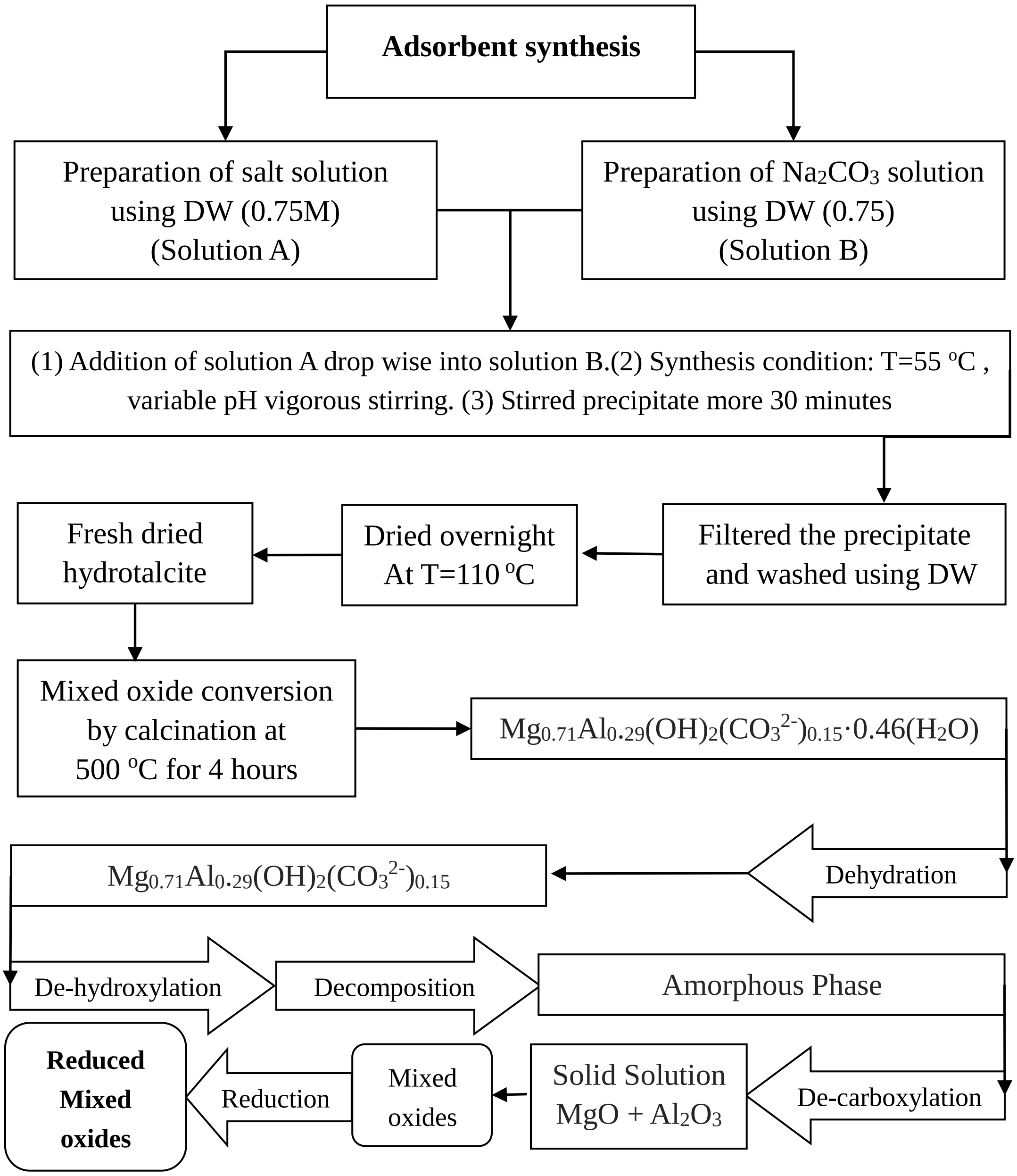


Figure 3: Synthesis of adsorbents by co-precipitation method

3.4 Chemicals and laboratory tools required

Chemicals and laboratory tools we required for project are listed as follows:

- **Chemicals :**
  1) Laboratory-scale pure hydrogen gas (H_2)
  2) Aluminum nitrate nonahydrate ($Al(NO_3)_3 \times 9H_2O$)
  3) Magnesium nitrate hexahydrate ($Mg(NO_3)_2 \times 6H_2O$)
  4) Nickel nitrate hexahydrate ($Ni(NO_3)_2 \times 6H_2O$)
  5) Sodium carbonate decahydrate ($Na_2CO_3 \times 10H_2O$)
  6) Lithium nitrate ($LiNO_3$)

- **Laboratory tools :**
  - I. Beaker
  - II. Hot plate
  - III. Vacuum filter setup
  - IV. Petri dish
  - V. Crucible

3.5 Experimentation

Three different adsorbents containing Li, Mg, Nil and Al have been prepared by using the co-precipitation method which had been described in the adsorbent synthesis part of the research. Synthesis temperature was maintained at 55 ^oC and molar ratio of metal precursors were Ni:Li:Al=1:2:1, Mg:Li:Al=1:2:1 and Li:Al=3:1. The fresh synthesized hydrotalcites were dried in the oven at 110 ^oC for one night in order to dehydrate and convert the hydrotalcite into powder form. The dried samples then were calcined at the temperature of 500 ^oC for 4 hours in order to convert them into mixed oxides of lithium, magnesium, nickel and aluminum, derived from the hydrotalcite. The hydrogen adsorption of adsorbent materials were measured at the temperature of 30^oC and the pressure of 0–760 mmHg using the equipment called micrometrics ASAP 2020C sorptometer. 20 mg of each sample was used to observe the hydrogen adsorption in the sorptometer. The samples were reduced by purging

H_2 gas at 20 mL/min in the vacuum condition, slowly increasing the temperature by 10 ^{o}C /min until it reaches 850 ^{o}C, then cooling it down back to 30 ^{o}C. For the adsorption test, 99.99% pure hydrogen gas was used. Analyses of hydrogen adsorption isotherm were conducted at 30 ^{o}C and the pressure range of 0–760 mmHg. The data for desorption isotherms were taken by performing evacuation at the same temperature of 30 ^{o}C by referring to the adsorption isotherm.

3.6 Characterization and adsorption test of adsorbents

The physio-chemical characteristics and morphologies of the synthesized adsorbents were characterized by the following analyzing methods and equipment:

i. **X- Ray Diffraction (XRD) Analysis**

The XRD Analysis is used as the main technique used to study the physical shape and thin layer and to identify the crystalline phase. Besides that, it also provided the unit of cell dimension, homogenized and average bulk of material composition.

ii. **Field Emission Scanning Electron Microscopy (FESEM) Analysis**

FESEM provides topographical and elemental information at magnifications of 10 times to 300,000 times, with virtually unlimited depth of field.

iii. **RAMAN Spectroscopy**

Spectroscopic technique is used to observe vibrational, rotational, and other low frequency modes in a system. It relies on inelastic scattering, or Raman scattering, of monochromatic light, from a laser in the visible, near infrared, or near ultraviolet range.

Adsorption analysis of the samples synthesized were investigated by the following equipment and technique:

iv. **Micromeritics ASAP 2020C adsorption apparatus**

Adsorption analysis provides information necessary to evaluate adsorption capacity of the the samples by measuring the amount of hydrogen gas adsorbed. Adsorbent samples can be tested at high temperatures reaching up to 1100 ℃ and pressures lower than 5-10 mmHg.

3.7 Gantt Chart and Key Milestones

Final Year Project I (September 2014)

🟪 **Process**

● **Milestone**

No.	Detail/ Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Selection of Project Topic	🟪	🟪												
2	FYP Briefing		🟪	🟪	🟪										
3	Preliminary Research Work		🟪	🟪	🟪	🟪									
4	Material and Equipment identification				🟪	🟪									
5	Submission of Extended Proposal						●								
6	Proposal Defence							🟪							
7	Project work continues								🟪	🟪	🟪	🟪	🟪		
8	Start Laboratory work													🟪	🟪
9	Submission of Interim Draft Report												●		
10	Submission of Interim Report													●	

Table 1: Gantt Chart for FYP1

Final Year Project II (January 2015)

No.	Detail/ Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Project Work Continues	🟪	🟪	🟪	🟪	🟪	🟪	🟪								
2	Submission of Progress Report							●								
3	Project Work Continues								🟪	🟪	🟪	🟪	🟪			
4	Pre-SEDEX										●					
5	Submission of Draft Final Report												●			
6	Submission of Dissertation (soft bound)													●		
7	Submission of Technical Paper													●		
8	Viva															●
9	Submission of Project Dissertation (Hard Bound)															●

Table 2: Gantt Chart for FYP2

Chapter 4

Results and discussion

This chapter discusses about the results obtained by referring to the experimental work that has been done. The results are divided into 3 main parts which are the adsorbent samples preparation, adsorbents characterization and finally checking the performance of adsorbents in the adsorption of hydrogen.

4.1 Adsorbent Preparation

This part discusses about the preparation of 3 samples of adsorbent with different metal content, starting by adsorbent sample calculation for co-precipitation synthesis till the adsorbent is formed. The amount of each sample and the sample components with different ratios are given.

Chemical Name	Symbol	Molecular Weight (g/mol)
$Ni(NO_3)_2 \times 6H_2O$	Ni	290.810
$Mg(NO_3)_2 \times 6H_2O$	Mg	256.330
$Al(NO_3)_3 \times 9H_2O$	Al	375.120
$LiNO_3$	Li	68.9500
$Na_2(CO_3)_2 \times 10H_2O$	Na	286.120

Table 3: Chemicals and their molecular weights

3 Samples

1)	Ni-Li-Al	1:2:1	(25 g)
2)	Mg-Li-Al	1:2:1	(25 g)
3)	Li-Al	3:1	(25 g)

The calculation is based on 25 gram of total weight of the adsorbent sample, by using metal precursors $Ni(NO_3)_2 \times 6H_2O$, $Mg(NO_3)_2 \times 6H_2O$ and $LiNO_3$ with their respective support of $Al(NO_3)_3 \times 9H_2O$ and precipitating agent $Na_2(CO_3)_2 \times 10H_2O$.

Ni-Li-Al (1:2:1)

Total weight = $Ni(NO_3)_2.6H_2O + LiNO_3 + Al(NO_3)_3.9H_2O = 734.88 g/mol$

$$Ni = \frac{1 \times 290.81}{734.88} \times 25 = 9.89\ g$$

$$Li = \frac{2 \times 68.95}{734.88} \times 25 = 4.69\ g$$

$$Al = \frac{1 \times 375.12}{734.88} \times 25 = 12.76\ g$$

Figure 4: Ni-Li-Al

Next is the calculation of required of total amount of $Na_2(CO_3)_2 \times 10H_2O$ for adsorbent sample. The formula given as below:

$W_T = W_1 + W_2 + W_3$

The respective weights are

W_1 = Required amount of $Na_2(CO_3)_2 \times 10H_2O$ for Ni precursor

W_2 = Required amount of $Na_2(CO_3)_2 \times 10H_2O$ for Li precursor

W_3 = Required amount of $Na_2(CO_3)_2 \times 10H_2O$ for Al support

Therefore,

$$W_T = 1.1 \times \left[\left(\frac{Weight\ of\ Ni}{MW}\right) + \left(\frac{Weight\ of\ Li}{MW}\right) + \left(\frac{Weight\ of\ Al}{MW} X \frac{2}{3}\right)\right] X\ MW\ of\ W$$

$$W_T = 1.1 \times \left(\frac{9.89}{290.81} + \frac{4.69}{68.95} + \frac{12.76}{375.12} \times \frac{2}{3}\right) \times 286.12 = 39.25g$$

Mg-Li-Al (1:2:1)

Total weight = $Mg(NO_3)_2 \times 6H_2O$ + $LiNO_3$+ $Al(NO_3)_3 \times 9H_2O$=700.4g/mol

$$Mg = \frac{1 \times 290.81}{700.4} \times 25 = 9.15\ g$$

$$Li = \frac{2 \times 68.95}{700.4} \times 25 = 4.92\ g$$

$$Al = \frac{1 \times 375.12}{700.4} \times 25 = 13.39\ g$$

Figure 5: Mg-Li-Al

Next is the calculation of required of total amount of $Na_2(CO_3)_2 \times 10H_2O$ for adsorbent sample. The formula given as below:

$W_T = W_1 + W_2 + W_3$

The respective weights are

W_1 = Required amount of $Na_2(CO_3)_2 \times 10H_2O$ for Mg precursor

W_2 = Required amount of $Na_2(CO_3)_2 \times 10H_2O$ for Li precursor

W_3 = Required amount of $Na_2(CO_3)_2 \times 10H_2O$ for Al support

Therefore,

$$W_T = 1.1 \times \left[\left(\frac{Weight\ of\ Mg}{MW}\right) + \left(\frac{Weight\ of\ Li}{MW}\right) + \left(\frac{Weight\ of\ Al}{MW}\ X\ \frac{2}{3}\right)\right] X\ MW\ of\ W$$

$$W_T = 1.1 \times \left(\frac{9.15}{256.33} + \frac{4.92}{68.95} + \frac{13.39}{375.12} \times \frac{2}{3}\right) \times 286.12 = 41.18\ g$$

Li-Al (3:1)

X + Y = 25g ------- (Equation 1)

$$\frac{X}{Molecular\ Weight\ X} + \frac{Y}{Molecular\ Weight\ Y} = 25\text{g}$$

$$\frac{X}{68.95} + \frac{Y}{375.12} = 3:1$$

$$\frac{X}{Y} \times \frac{375.12}{68.95} = 3:1$$

$$\frac{X}{Y} = 3\ (0.184)$$

X = 0.55 Y------- (Equation 2)

Figure 6: Li-Al

Substitute Equation 2 into Equation 1

0.55 Y + Y = 25g ⇨ 1.55 Y = 25g ⇨ Y = 16.13 g

X= 25g – 16.13g ⇨ X = 8.87 g

$W_T = W_1 + W_2$

The respective weights are

W_1= Required amount of $Na_2(CO3)_2$×10H2O for Li precursor

W_2 = Required amount of $Na_2(CO3)_2$×10H2O for Al support

Therefore,

$$W_T = 1.1 \times \left[\left(\frac{Weight\ of\ Li}{MW}\right) + \left(\frac{Weight\ of\ Al}{MW} X\ \frac{2}{3}\right)\right] X\ MW\ of\ W$$

$$W_T = 1.1 \times \left(\frac{8.87}{68.95} + \frac{16.13}{375.12} \times \frac{2}{3}\right) \times 286.12 = 49.31\ g$$

Molar Ratios	Nickel (Ni)	Magnesium (Mg)	Lithium (Li)	Aluminum (Al)
Ni:Li:Al (1:2:1)	9.89 g	-	4.69 g	12.76 g
Mg:Li:Al (1:2:1)	-	9.15 g	4.92 g	13.39 g
Li:Al (3:1)	-	-	8.87 g	16.13 g

Table 4: Weight of chemicals used based on the molar ratio

4.2 Characterization of prepared adsorbents

For identification of the surface structure, physio-chemical characteristics and morphologies of the adsorbent samples, 3 types of characterization techniques were used which are Raman spectroscopy, XRD and FESEM.

4.2.1 Raman spectroscopy

Raman spectroscopy shows the fingerprints of the material in the sample. The material in the sample may consist of one or several components. Simply it provides the quality and quantity of the materials in the sample. The qualitative analysis of the adsorbent samples can be investigated by referring to the sample spectrum and

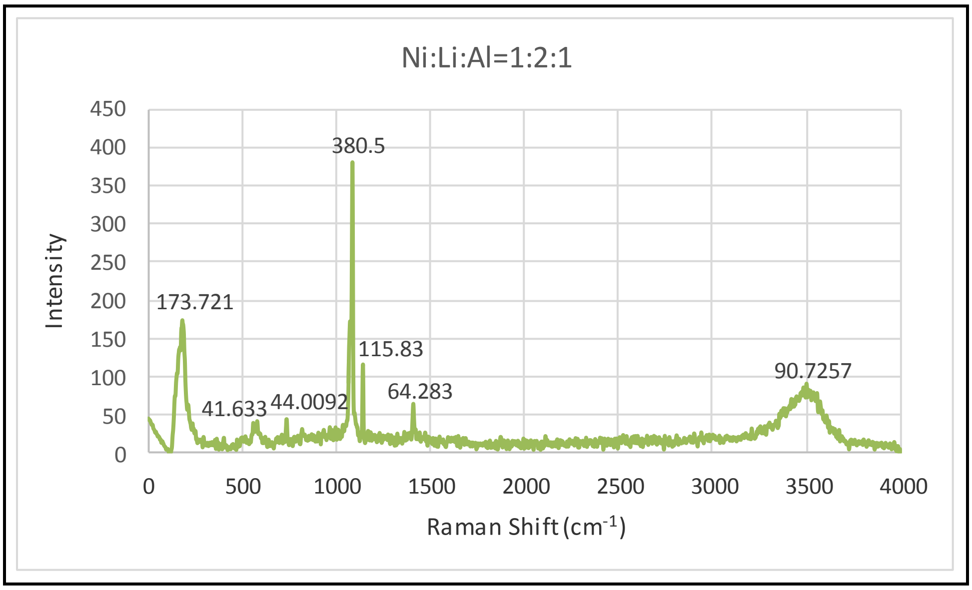


Figure 7: Raman spectra of adsorbent Ni:Li:Al

comparing with the reference spectra. Raman spectra of adsorbent Ni:Li:Al with composition of 1:2:1 is shown in Figure 7 which shows several Raman shifts. Raman shifts at the intensities of 173.721, 41.633, 44.0092, 380.5, 115.83, 64.283 and 90.7257 cm^{-1} ensured the formation of the mixed oxides of Li_2O, NiO and Al_2O_3. Raman spectra of adsorbent Mg:Li:Al with composition of 1:2:1 is shown in the Figure 8. It can be observed that the Raman shift of this adsorbents have almost the same band of Raman shift with different intensity which shows that the composition of both adsorbents has common mixed oxides. Raman shifts at the intensities of 373.386, 82.2384, 829.492, 170.63 and 138.09 cm^{-1} verified the formation of the

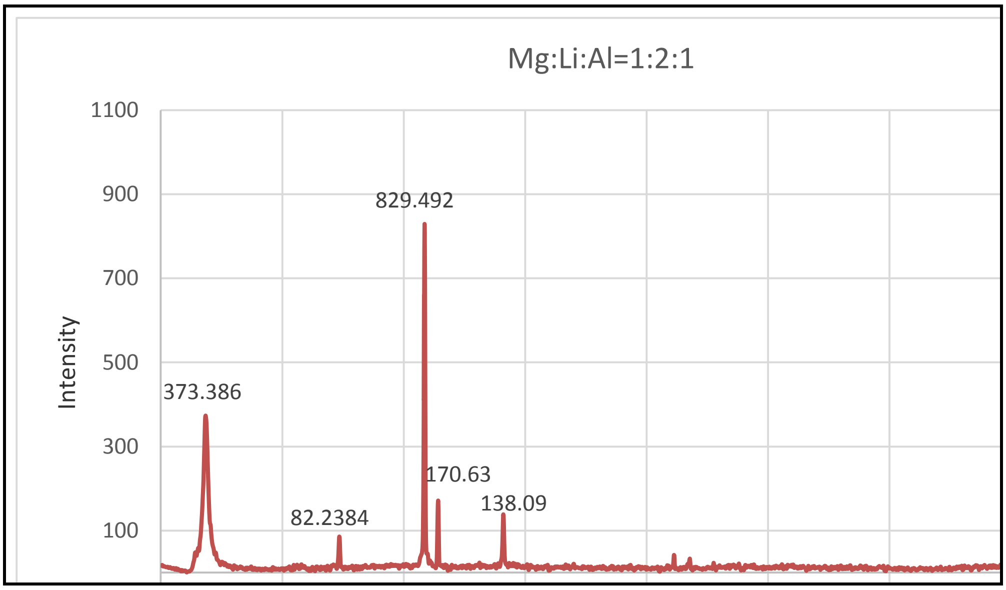


Figure 8: Raman spectra of adsorbent Mg:Li:Al

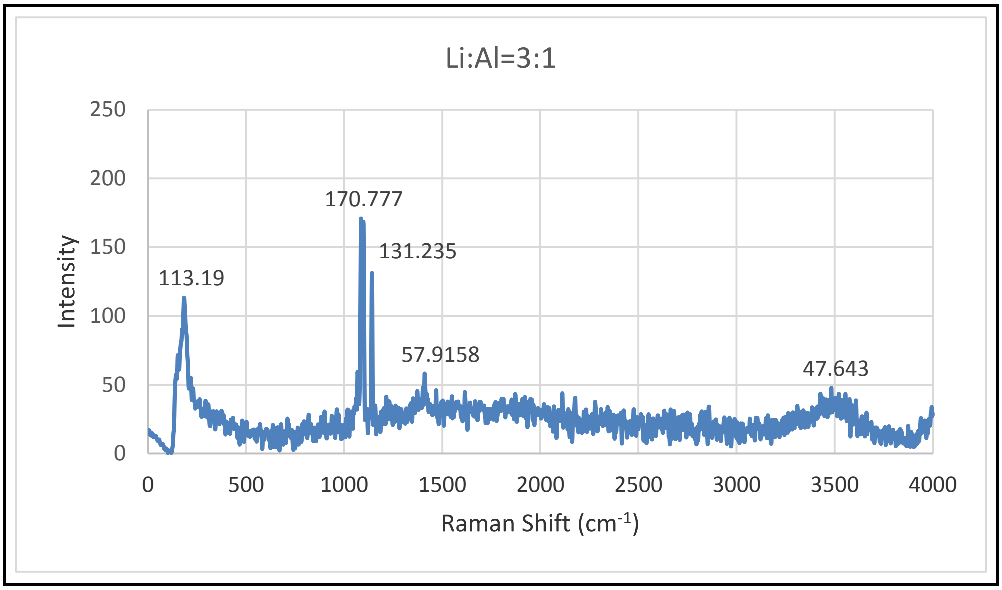


Figure 9: Raman spectra of adsorbent Li:Al

mixed oxides of MgO, Li_2O and Al_2O_3. The Raman spectra of adsorbent Li:Al with composition of 3:1 is shown in Figure 9. This adsorbent has a Raman shift at the intensities of 113.19, 170.777, 131.235, 57.9158 and 47.643. By referring to the spectra libraries, this justifies that the adsorbent has a mixed oxides of the Li_2O and Al_2O_3. Raman shift band is different for each material where it gives a qualitative analysis about the sample. All the three adsorbents have a common Raman shift bands which shows the similarity in the composition where the presence of the same mixed oxides can be observed in each of them. The difference is in the intensity of the molecular vibration which shows the quantity of each component in the sample. By referring to the same Raman shift of the three sample, we can observe the difference in the quantity of mixed oxides. The common Raman shifts in all three samples occur at the band of 180-200 and 1050-1150 cm^{-1} which represents the band of most common mixed oxides, Li_2O and Al_2O_3 respectively. Also MgO at 1410 and NiO at 3500 cm^{-1}.

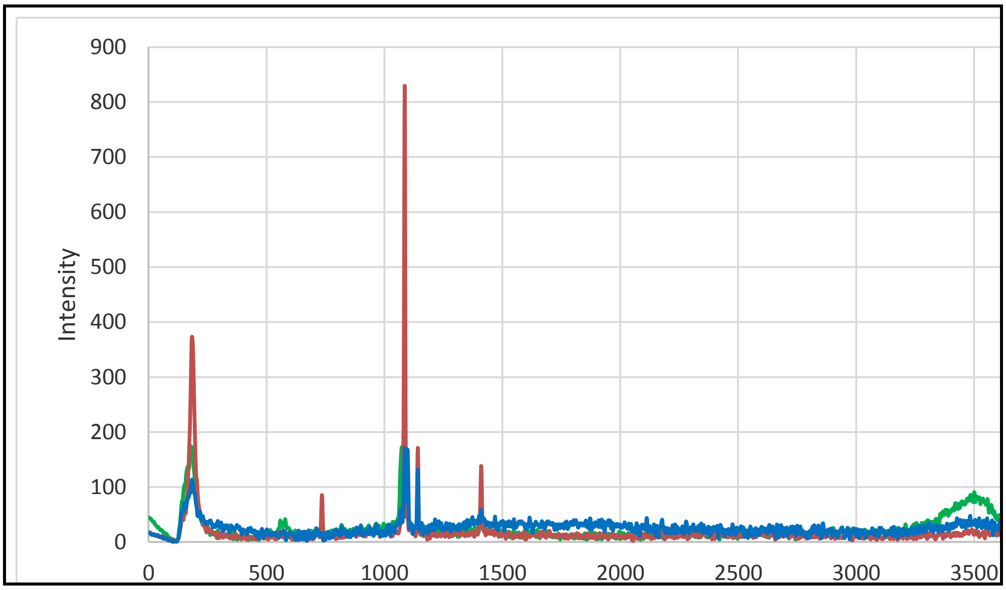


Figure 10: Mixed Raman spectra

4.2.2 X-ray diffraction

XRD patterns for mixed oxides show that the precursors of the synthesized hydrotalcite decomposed fully in calcination stage at the temperature of 500 ˚C and led to the formation of different oxide derivatives. The XRD results are compared with reference powder distraction standards and the composition was identified.

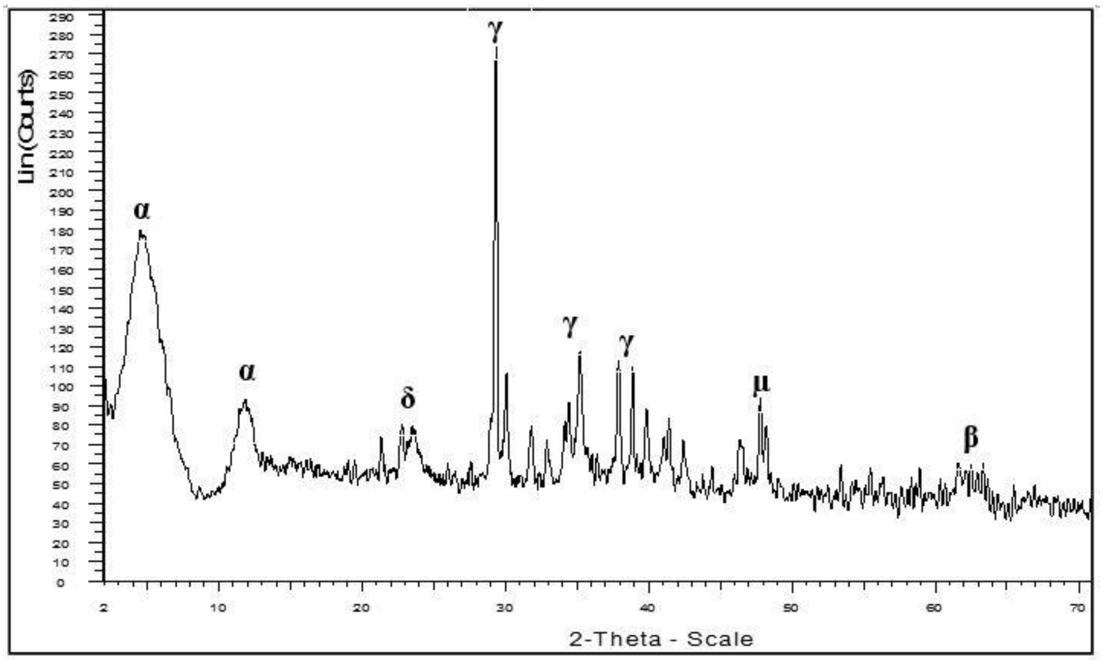


Figure 11: XRD pattern of Ni:Li:Al mixed oxide (Symbols indicate: LiO_2 = 'α', $LiAlO_2$ = 'δ', NiO = 'μ', $NiAl_2O_4$ = 'β', Al_2O_3 ='γ')

Oxides of the samples were symbolized with different symbols. The XRD pattern for the sample Ni:Li:Al is given in the Figure 11. It shows the formation of oxides like LiO_2, $LiAlO_2$, NiO, NiAl2O4 and Al_2O_3. The same observations can be done from the XRD patterns of the samples Mg:Li:Al and Li:Al. The XRD pattern of the sample

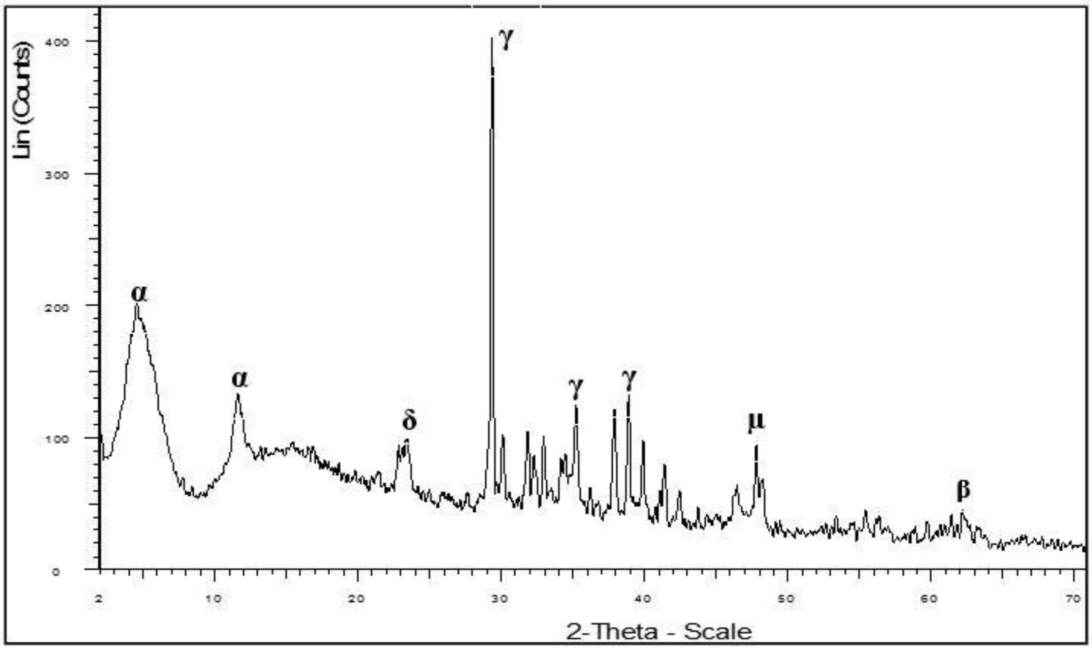


Figure 12: XRD pattern of Mg:Li:Al mixed oxide (Symbols indicate: LiO_2 = 'α', $LiAlO_2$ = 'δ', MgO = 'μ', $MgAl_2O_4$ = 'β', Al_2O_3 ='γ')

Mg:Li:Al shows the formation of oxides which are LiO_2, $LiAlO_2$, MgO, $MgAl_2O_4$ and Al_2O_3. The pattern is shown in the Figure 12. The XRD pattern of the Li:Al is almost similar to the previous two sample patterns where it only has the oxides of LiO_2, $LiAlO_2$ and Al_2O_3. The pattern is given in the Figure 13.

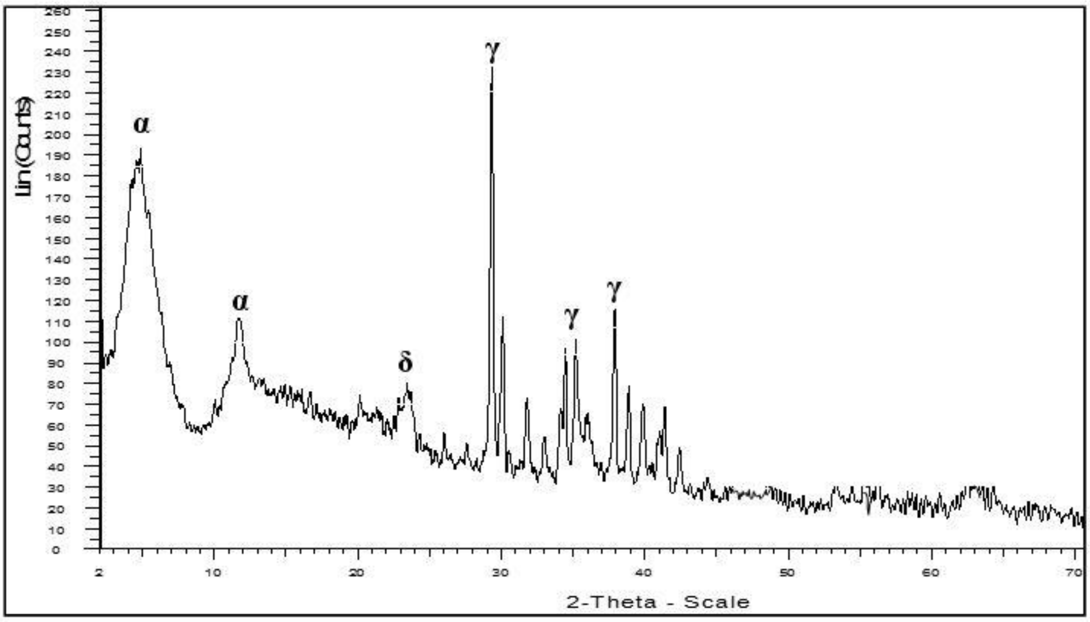
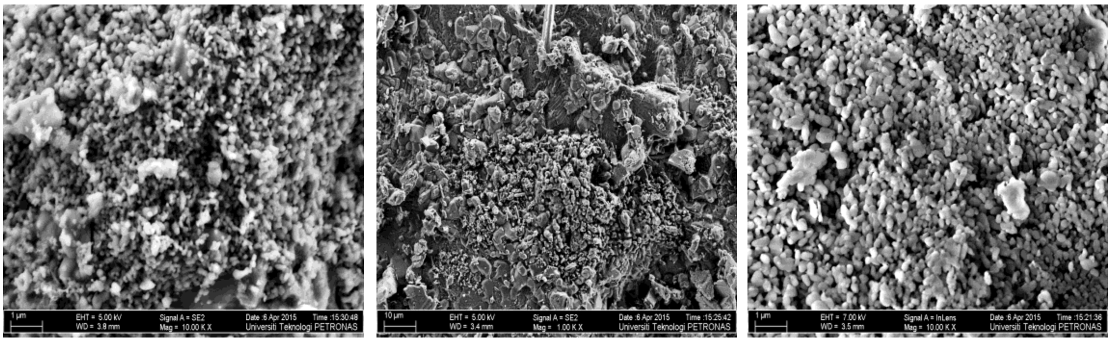


Figure 13: XRD pattern of Li:Al mixed oxide (Symbols indicate: LiO_2 = 'α', $LiAlO_2$ = 'δ', Al_2O_3 ='γ')

All the three XRD patterns have overlapping, which shows an abundancy of two main mixed oxides of LiO_2 and Al_2O_3 derived from the hydrotalcite. Analysis of XRD results shows that the derived mixed oxides are homogenous. The formation of mixed oxides from the calcination is a crucial part for preparing adsorbent, as they were reduced to form reduced mixed oxides. Reduced mixed oxides of LiO_2, MgO, NiO and Al_2O_3 are the components which can capture the hydrogen. Three different combination of these metal precursors were tested in hydrogen adsorption to find out best combination with highest storage capacity.

4.2.3 Field Emission Scanning Electron Microscopy (FESEM)

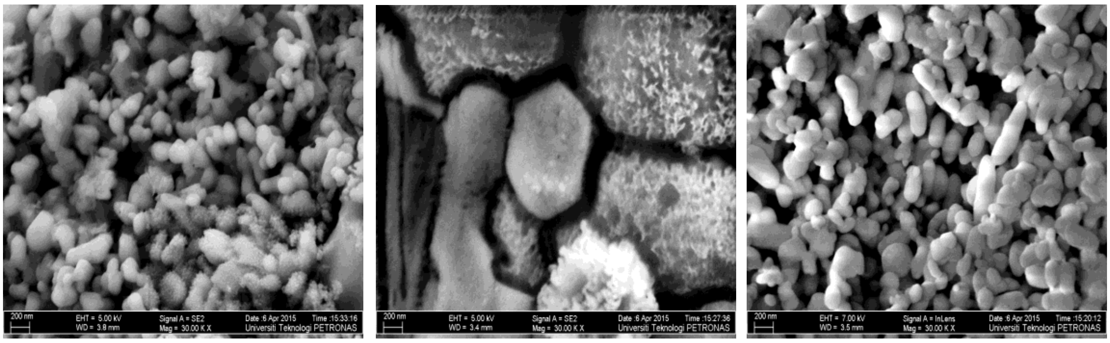
Analysis using Field Emission Scanning Electron Microscopy was conducted by using Philips XL30/FEI ESEM which operates at an accelerating voltage from 5 to 30kv. The FESEM images were taken at 10000x and 30000x magnifications. The images taken by FESEM represents the surface morphology of the adsorbents in the mixed oxide form. The images of three different adsorbents are shown with varying magnification as follows in the Figures 14, 15.



(a) (b) (c)

Figure 14: Images of mixed oxides at 10000x magnification:

(a) Li:Al, (b) Mg:Li:Al , (c) Ni:Li:Al

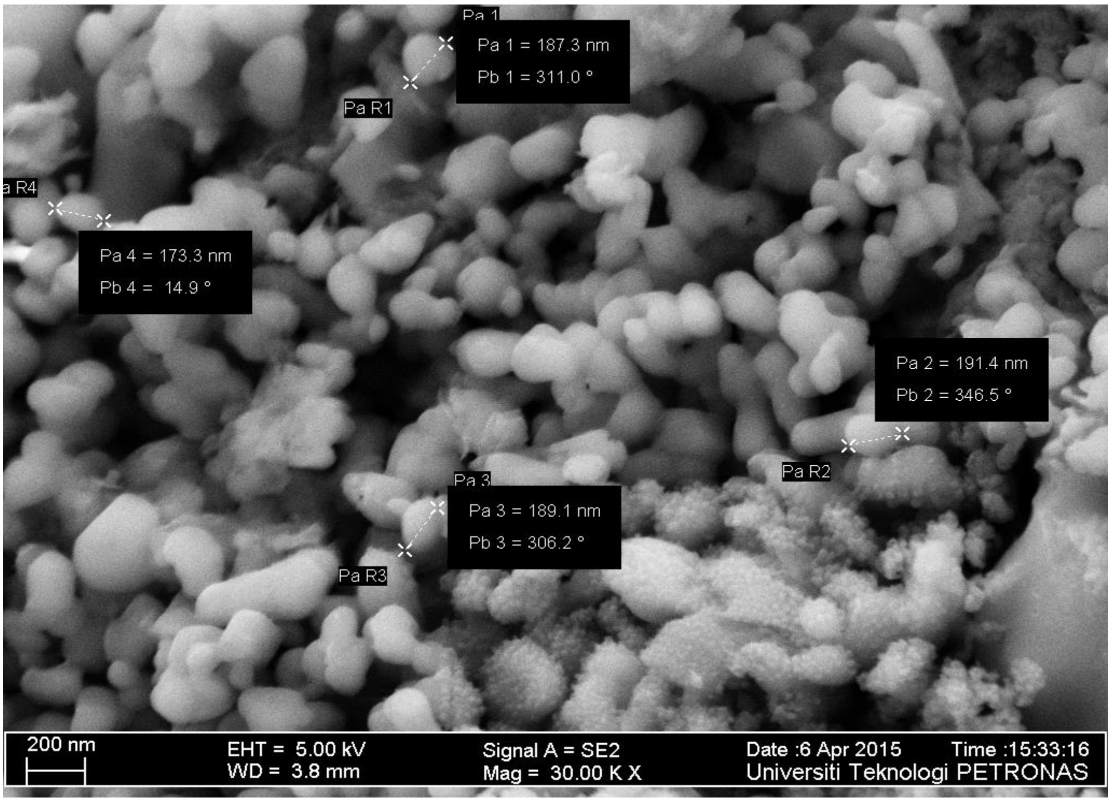


(a) (b) (c)

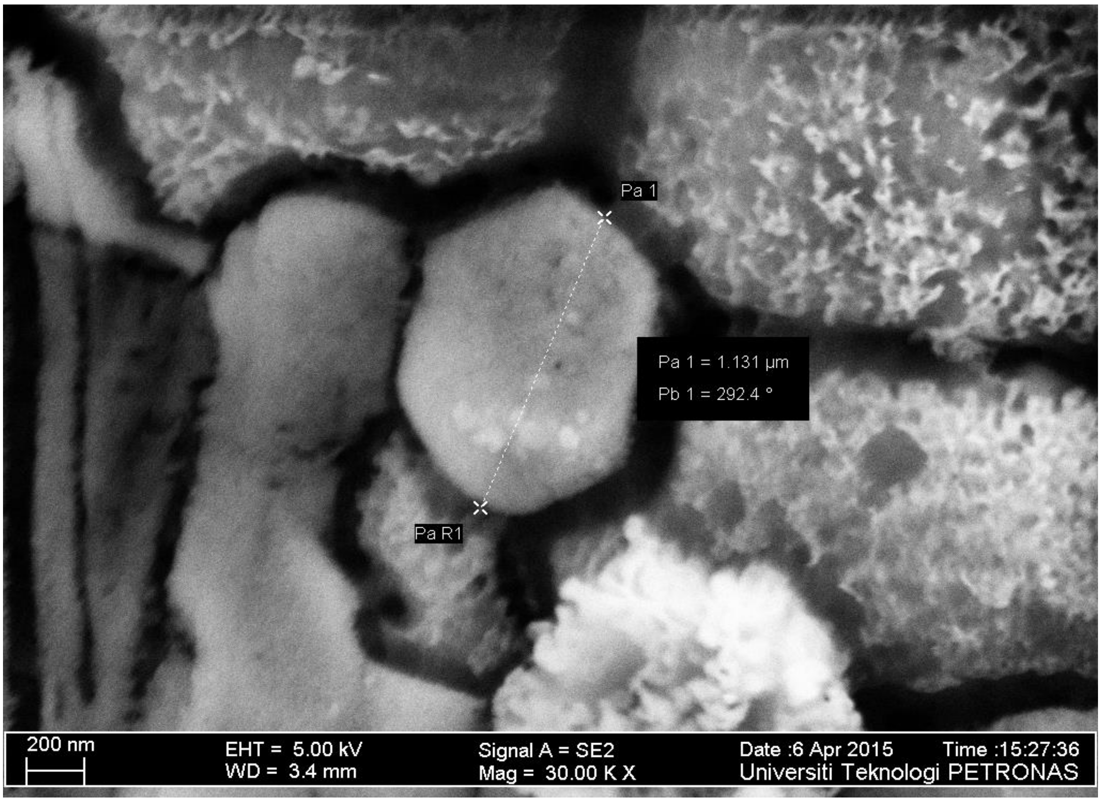
Figure 15: Images of mixed oxides at 30000x magnification:

(a) Li:Al, (b) Mg:Li:Al , (c) Ni:Li:Al

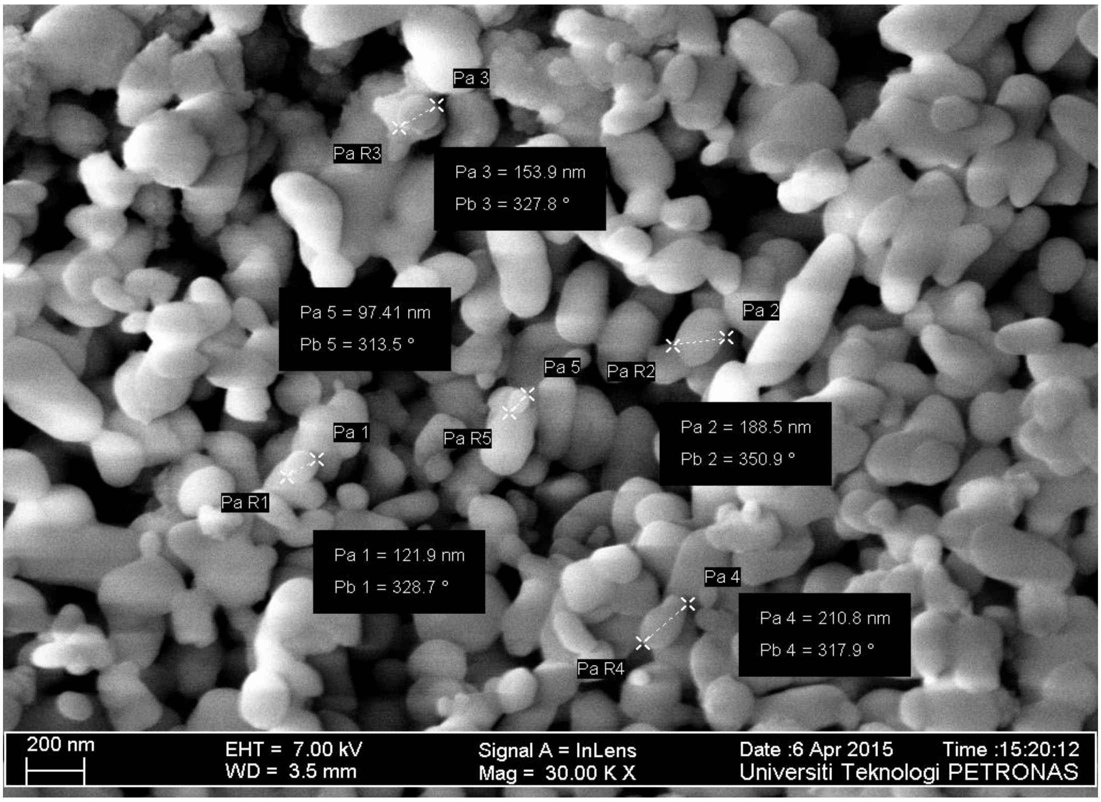
FESEM images above show that the Mg:Li:Al adsorbent is formed in the polygonal shape while the Li:Al and Ni:Li:Al demonstrated spherical and oval shaped structure. Small particle size and large surface area are the main factors for the development of highly hydrogen concentrated adsorbent because small particle size has a tendency to obtain highly saturated surface concentration but exhibit slow response to desorption. By referring to the particle sizes of the adsorbents, it is clear that the combination of Mg:Li:Al has a higher particle size diameter compared to others. Comparing the average sizes of all particles in the samples, it is found to be that the


Pa 1
Pa 1 = 187.3 nm
Pb 1 = 311.0 °
Pa R1
a R4
Pa 4 = 173.3 nm
Pb 4 = 14.9 °
Pa 2 = 191.4 nm
Pb 2 = 346.5 °
Pa R2
Pa 3
Pa 3 = 189.1 nm
Pb 3 = 306.2 °
Pa R3
200 nm
EHT = 5.00 kV
WD = 3.8 mm
Signal A = SE2
Mag = 30.00 K X
Date :6 Apr 2015
Time :15:33:16
Universiti Teknologi PETRONAS

(a)


Pa 1
Pa 1 = 1.131 µm
Pb 1 = 292.4 °
Pa R1
200 nm
EHT = 5.00 kV
WD = 3.4 mm
Signal A = SE2
Mag = 30.00 K X
Date :6 Apr 2015
Time :15:27:36
Universiti Teknologi PETRONAS

(b)



(c)

Figure 16: Images of mixed oxides at 30000x magnification with particle sizes:

(a) Li:Al, (b) Mg:Li:Al , (c) Ni:Li:Al

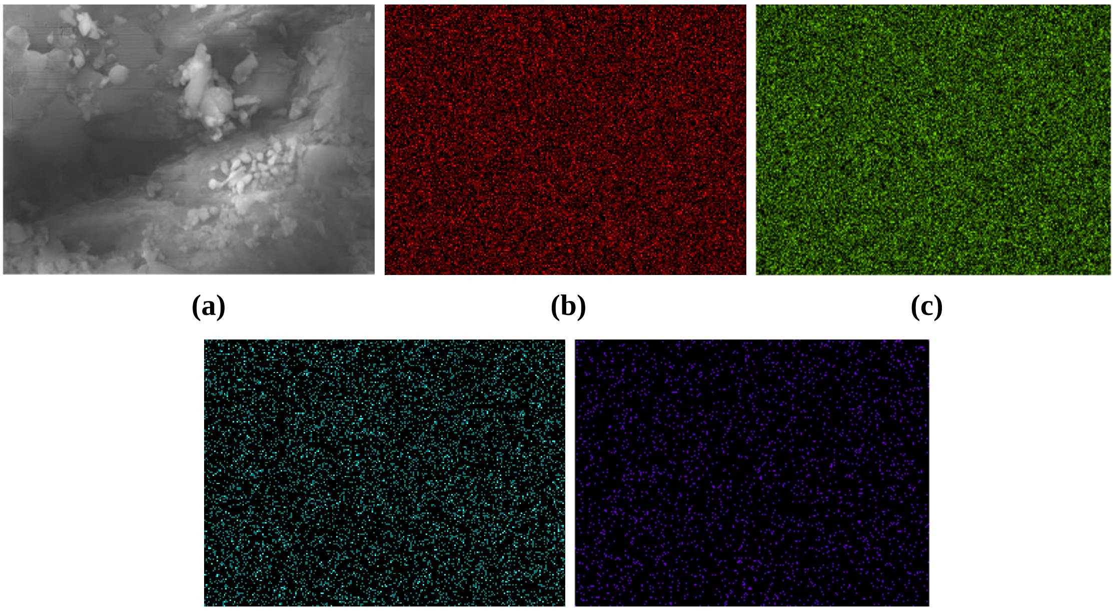
sample Ni:Li:Al has the smallest average size of particle among the adsorbents. Average size is 154.502 nm. Smaller particles ensures better adsorption isotherm. Also Ni:Li:Al has a more space between particles, which can ensure better hydrogen molecule adsorption with its higher void fraction.

4.2.4 Energy Dispersive X-ray Spectroscopy (EDX) Analysis

In order to find out more information about adsorbent surface structure, Energy Dispersive X-ray Spectroscopy (EDX) mapping was conducted to find out the dispersion of magnesium, nickel and aluminum on the component surface. Because of small molecule size of lithium, the instrument is incapable of providing the dispersion of the molecule on the adsorbent surface. EDX analysis was conducted by using the same equipment as with FESEM, which is Philips XL30/FEI ESEM. The main purpose is to find out the actual and uniform dispersion of magnesium, nickel and aluminum. Also the component contains sodium, carbon and oxygen. Moreover, the atomic percentage of each element was investigated by EDX mapping to find out whether the right amount of metal precursors were used to synthesize the adsorbent by using co-precipitation method. Any mismatches on theoretical and experimental values would be noted for further improvement on preparation of adsorbent in the future studies. EDX analysis results are shown below:

Atomic Number	Element	Weight Percentage (%)	Atomic Percentage (%)
13	Aluminum	18.18	7.39
8	Oxygen	35.51	49.69
11	Sodium	36.19	27.99
6	Carbon	10.12	14.93
Total		100	100

Table 5: Weight and Atomic Percentage of Elements for Li:Al adsorbent


(a) **(b)** **(c)**

(d) **(e)**

Figure 17: Li:Al adsorbent surface component dispersion: (a) Electron image, (b) Oxygen, (c) Sodium, (d) Aluminum, (e) Carbon

Atomic Number	Element	Weight Percentage (%)	Atomic Percentage (%)
13	Aluminum	1.53	0.98
8	Oxygen	55.42	59.85
6	Carbon	10.01	14.40
11	Sodium	31.50	23.67
12	Magnesium	1.54	1.09
Total		100	100

Table 6: Weight and Atomic Percentage of Elements for Mg:Li:Al adsorbent

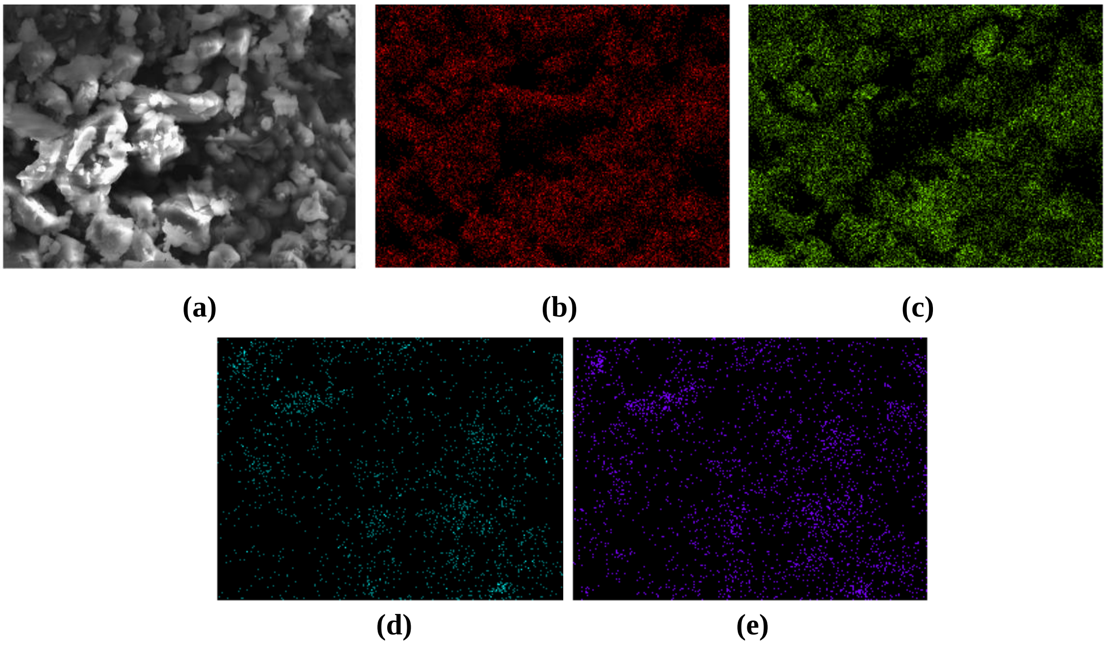


Figure 18: Mg:Li:Al adsorbent surface component dispersion: (a) Electron image, (b) Oxygen, (c) Sodium, (d) Magnesium, (e) Aluminum

Atomic Number	Element	Weight Percentage (%)	Atomic Percentage (%)
13	Aluminium	4.29	2.85
8	Oxygen	48.70	54.65
28	Nickel	7.88	2.41
6	Carbon	13.35	19.96
11	Sodium	25.77	20.12
Total		100	100

Table 7: Weight and Atomic Percentage of Elements for Ni:Li:Al adsorbent

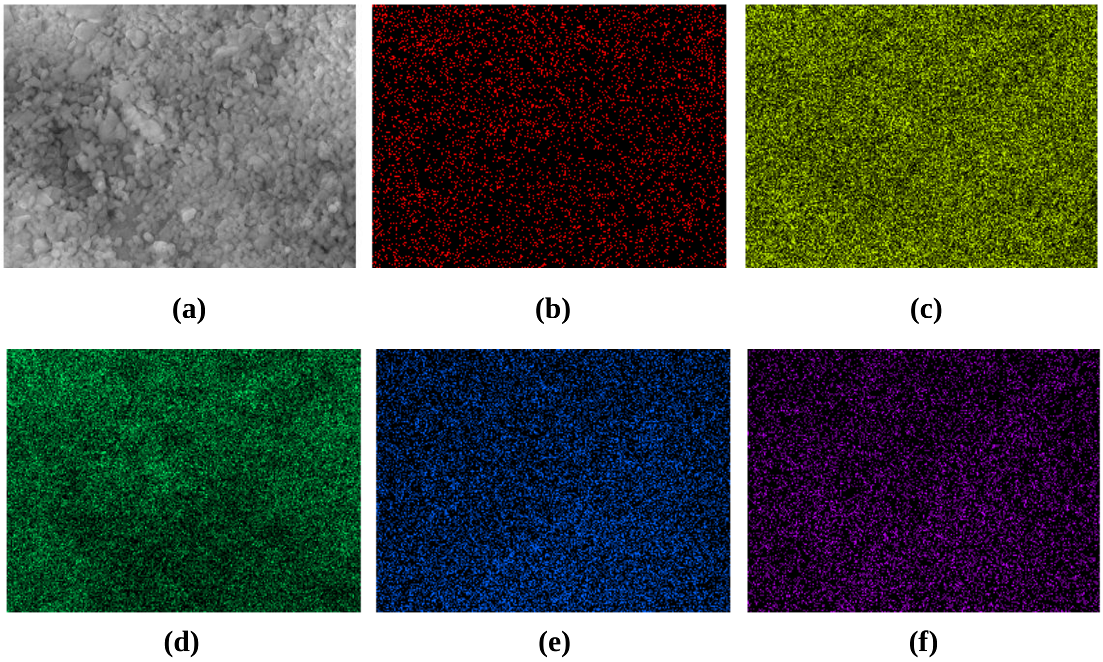


Figure 19: Ni:Li:Al adsorbent surface component dispersion: (a) Electron image, (b) Carbon, (c) Oxygen, (d) Sodium, (e) Aluminum, (f) Nickel

EDX mappings results above show that magnesium and nickel combined in a perfect way based on the molar ratio for the adsorbents. The uniform dispersion of the metal precursors enhances adsorption capacity and therefore enables for more hydrogen to be captured. Even though the EDX mapping and weight percent is not shown for lithium, it can be assumed that it achieved its high dispersion and combination with other metals based on our EDX results. The amount of lithium can be taken from the sample preparation part for the reference.

Results show that adsorbent samples have big amount of sodium and oxygen. Presence of such a big amount of sodium is reasonable since sodium carbonate decahydrate was used as precipitating agent for all adsorbent samples during the synthesis. Presence of oxygen in each adsorbent sample is justified from the formation of mixed oxides where the oxygen is the main part of it. Most of the oxygen has been removed during the calcination stage of adsorbent synthesis.

EDX analysis proved that all adsorbent samples were successfully synthesized by co-precipitation method which is necessary for better adsorption results.

4.3 Adsorption analysis

Adsorption analysis was conducted on each adsorbent sample by using Micromeritics ASAP 2020C adsorption apparatus. The isotherm of the sample Ni:Li:Al is shown in the Figure 20. The isotherm shows that the amount of hydrogen adsorbed for the first analysis is about 4.5 cm^3/g. Desorption capacity of the sample was analyzed by purging nitrogen gas in order to remove hydrogen from the sample surface structure. The same quantity of hydrogen was fed into adsorption unit. The isotherm plot of repeat analysis showed the amount of hydrogen adsorbed to be not more than 4.1 cm^3/g. This shows that the 0.4 cm^3/g of hydrogen gas has undergone chemical adsorption (chemisorption) with the mixed oxides of NiO, LiO_2 and Al_2O_3.

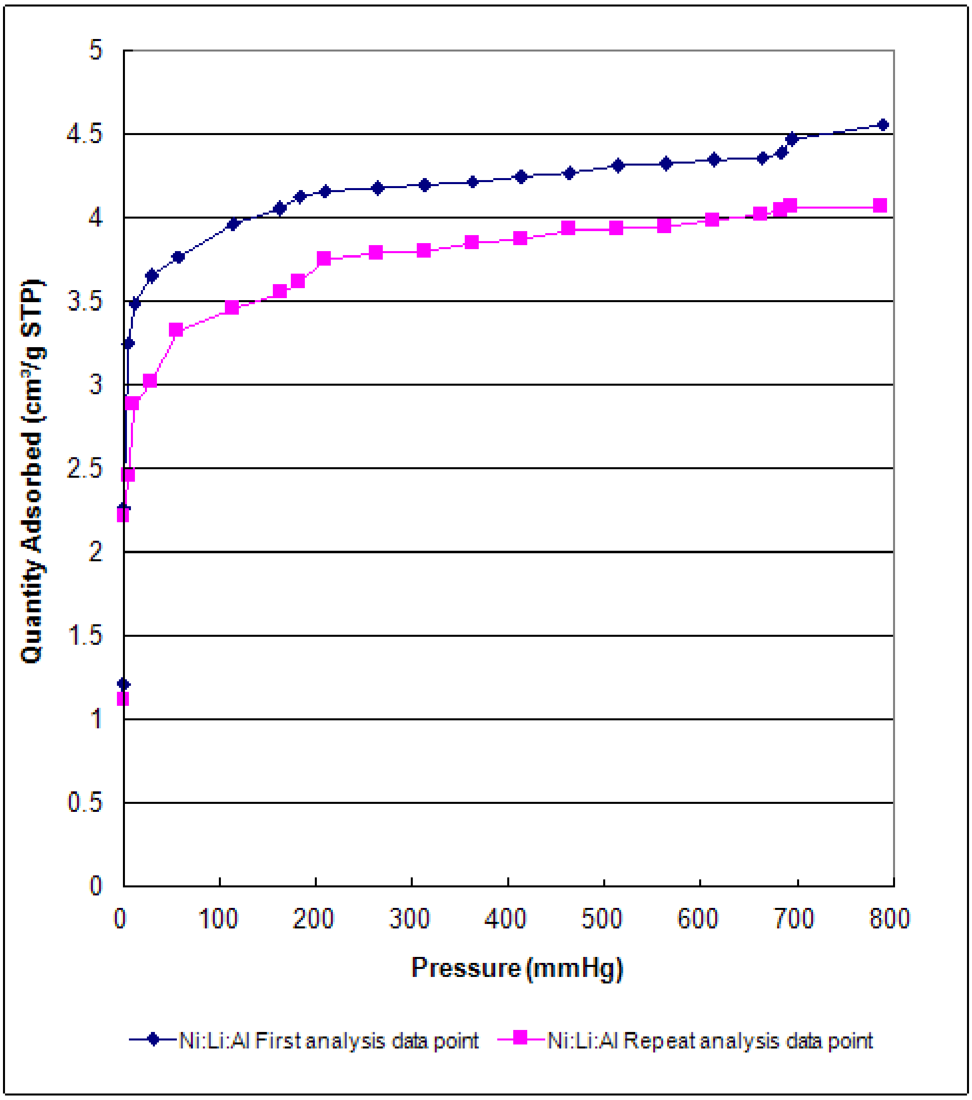


Figure 20: Isotherm plot for Ni:Li:Al adsorbent

Chemisorbed portion of hydrogen has formed the hydrides with the mixed oxides of Ni:Al:Li sample and cannot be recovered. Desorption capacity of the adsorbent sample Ni:Al:Li can be identified by the amount of hydrogen which has undergone physisorption with adsorbent, that is 4.1 cm^3/g.

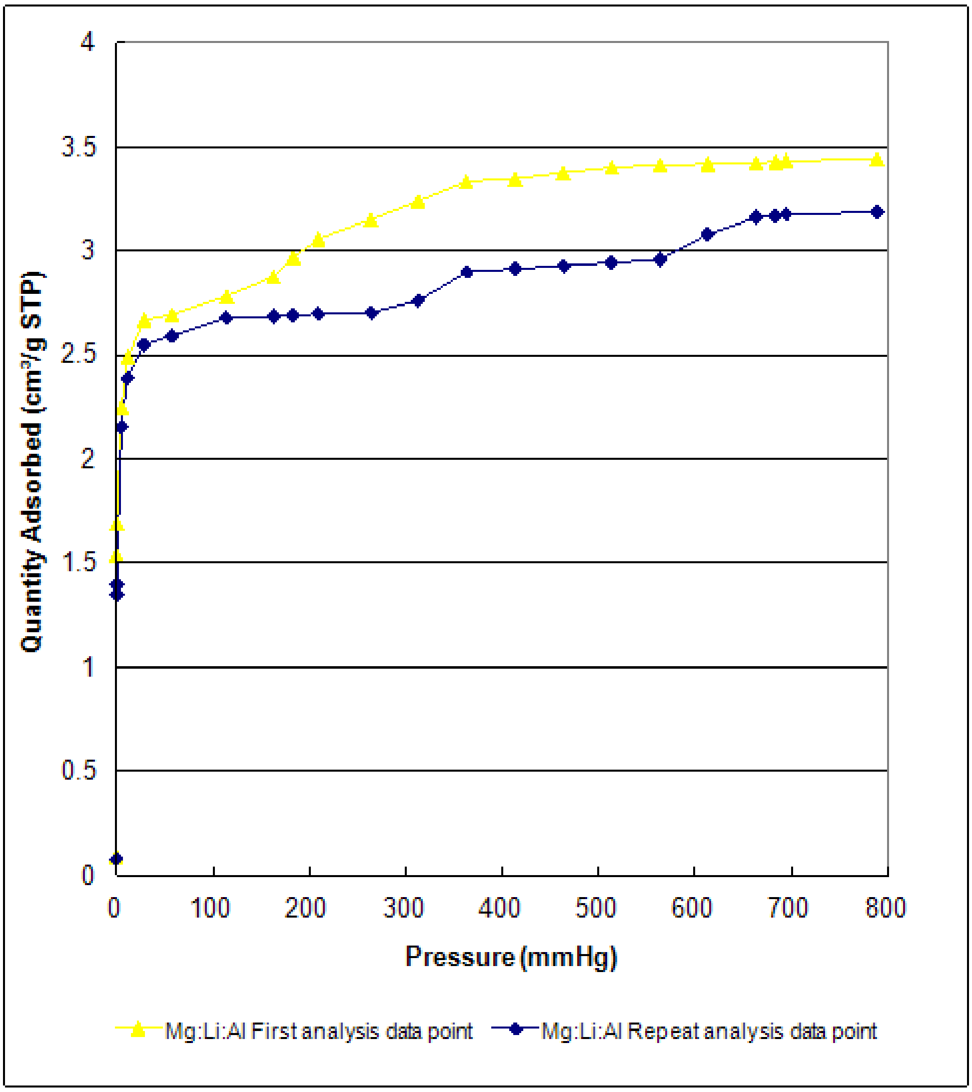


Figure 21: Isotherm plot for Mg:Li:Al adsorbent

The Figure 21 shows the isotherm plot for Mg:Li:Al adsorbent with first analysis data of approximately 3.44 cm^3/g. The isotherm plot of repeat analysis showed the amount of hydrogen adsorbed to be approximately 3.20 cm^3/g. The amount of hydrogen reacted with mixed oxides of MgO, LiO_2 and Al_2O_3 is about 0.24 cm^3/g. The data for Mg:Li:Al adsorbent shows higher hydrogen wt% desorption capacity compared to Ni:Li:Al adsorbent. Nevertheless, its adsorption capacity is smaller.

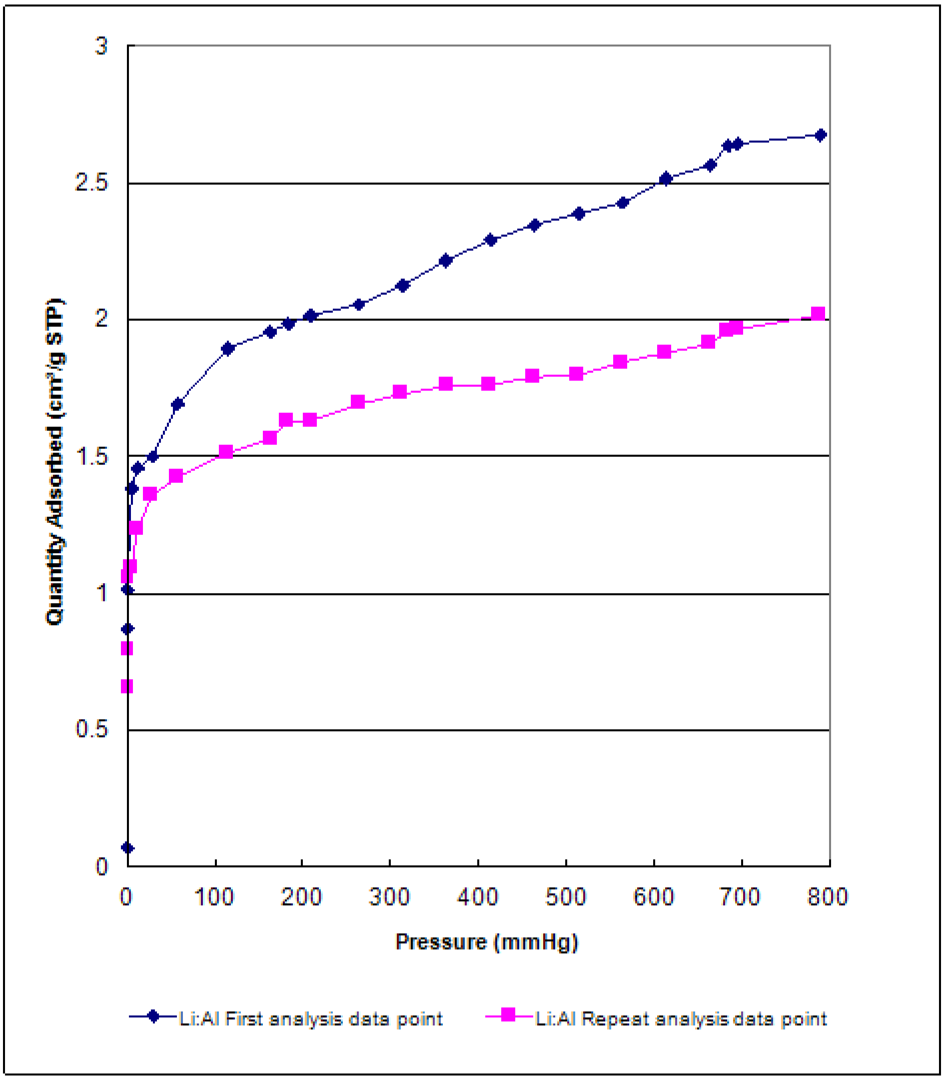


Figure 22: Isotherm plot for Li:Al adsorbent

The Figure 22 shows the isotherm plot for Li:Al adsorbent with first analysis data of approximately 2.67 cm^3/g. The isotherm plot of repeat analysis showed the amount of hydrogen adsorbed to be approximately 2.01 cm^3/g. The amount of hydrogen chemically adsorbed by mixed oxides of LiO_2 and Al_2O_3 is about 0.66 cm^3/g, which is the lowest hydrogen desorption capacity among the adsorbents. Also it possesses the lowest adsorption capacity as well.

Overall results showed that Ni:Li:Al has a highest adsorption isotherm compared to other two adsorbent materials. The small particle size and high porous property of Ni:Li:Al proves the presumption of FESEM. The results of XRD and Raman were proved by the presence of mixed oxides, the major components of adsorbents.

Chapter 5

Conclusion and Recommendation

5.1 Conclusion

This chapter discusses about the conclusions of the overall project including the recommendation for future study. The purpose of this project is to fulfil the 2 main objectives which is stated below:

1) To prepare/derive highly hydrogen concentrated metal hydride from clay based materials.
2) To evaluate the performances of adsorbents for their adsorption and desorption capacity.
3) To characterize the adsorbent materials using XRD, FESEM and RAMAN.

Based on the project objectives, all the tasks have been successfully achieved. For the objective (1), co-precipitation method has been implemented in order to produce hydrotalcite derived adsorbent material. For objective (2) Adsorption analysis was conducted by using Chemisorption reactor to find out the best adsorbent metal combination which has a high hydrogen adsorption and desorption capacity. Besides that, for objective (3), RAMAN Spectroscopy, XRD and FESEM characterizations have been conducted to investigate the physio-chemical characteristics and morphologies of adsorbent samples. Based on the results obtained from the overall project, it was found that the combination of Ni:Li:Al is the best adsorbent to be used for the storage of high amount of hydrogen. Its adsorption capacity and desorption capacity is found to be 4.5 cm^3/g and 4.1 cm^3/g respectively.

5.2 Recommendation

As the research based on the storage of hydrogen metal hydride is indefinitely wide, various future works can be performed to extend the research work to ensure more promising outcome. For the development of a better adsorbent which can adsorb and desorb more hydrogen, continuous research work has to be performed in the laboratory scale to explore the possible ways to optimize the adsorption and desorption process.

The recommendations will be to explore different metallic combination that can capture more hydrogen. And also the scope of the project that is going to be given for any candidate has to be feasible enough to accomplish it in the given time constrain.

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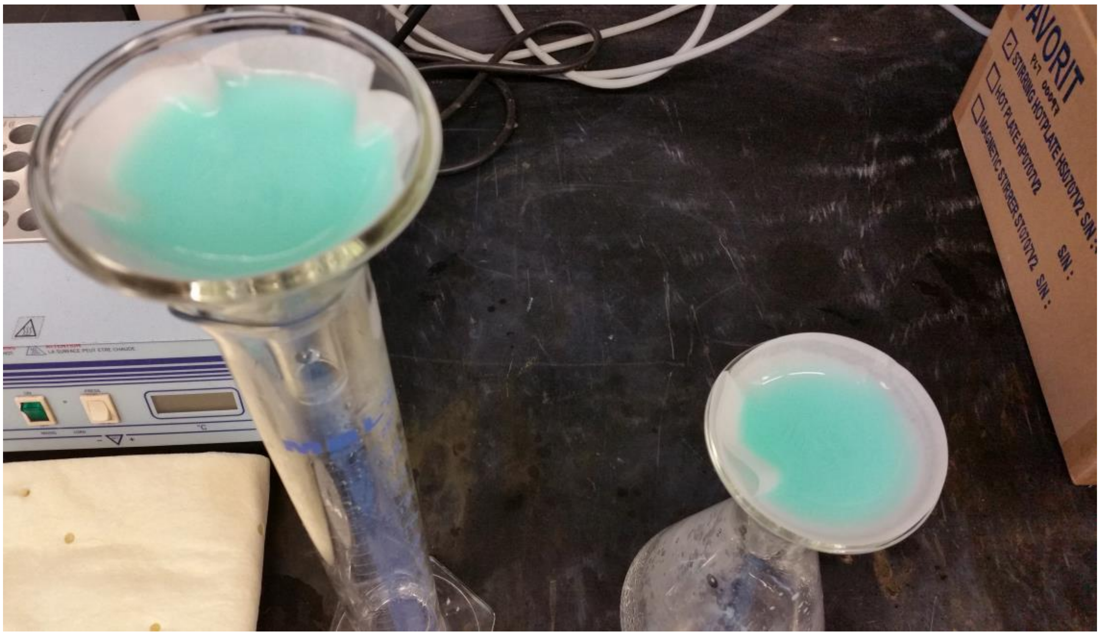
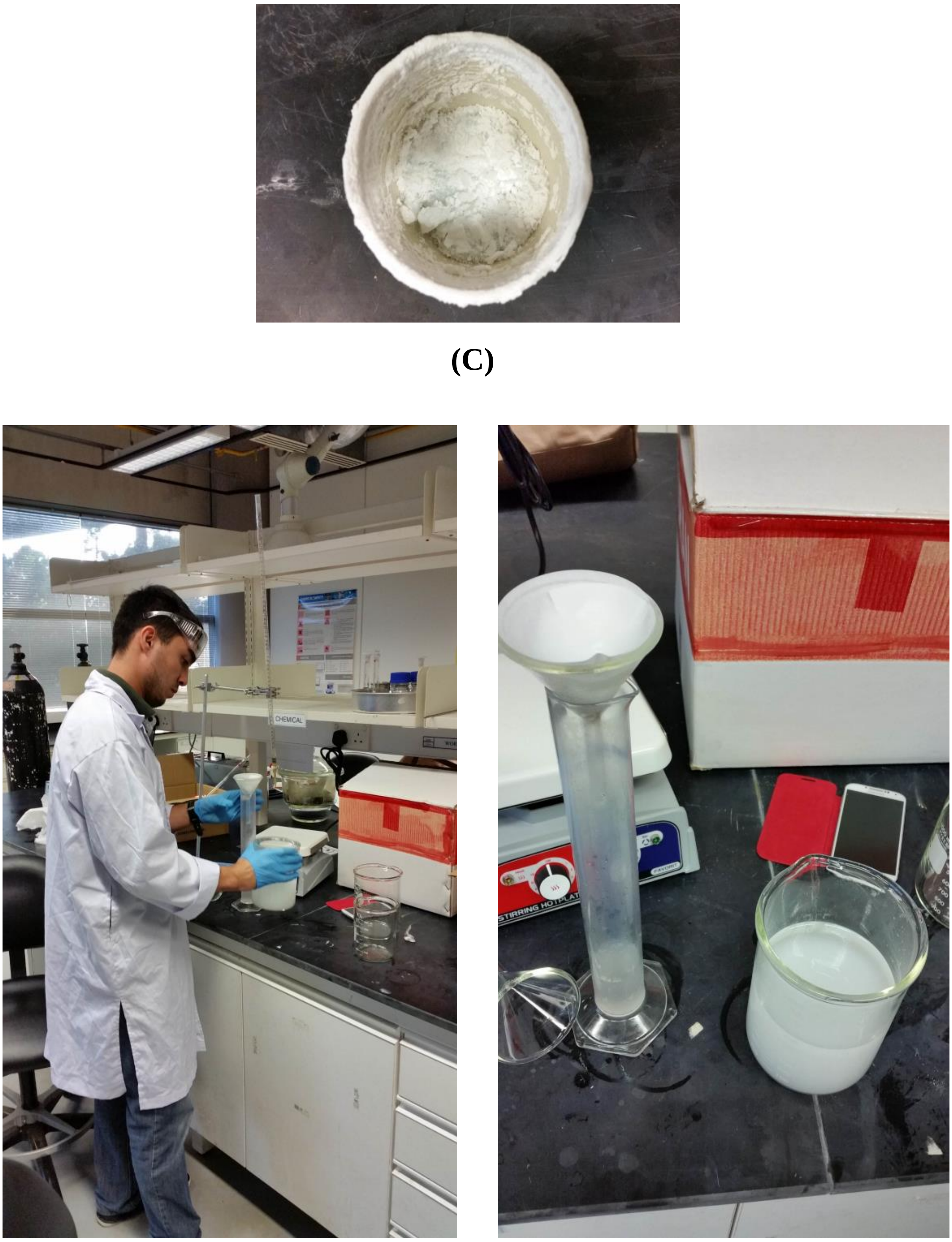
APPENDICES



(a)

(b)



(C)

(d)

(e)

Figure A1: Adsorbent synthesis via co-precipitation method