STUDY ON SORPTION OF MOISTURE BY THE *ANADARA GRANOSA* WASTE

by

NUR AINDA BINTI MOHD BUKHARI

Dissertation submitted in partial fulfillment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

SEPTEMBER 2013

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
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CERTIFICATION OF APPROVAL

Study on Sorption of Moisture by *Anadara Granosa* Waste

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Nur Ainda binti Mohd Bukhari

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfillment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

____
(Mr Zamri Abdullah)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
September 2013

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.

NUR AINDA BINTI MOHD BUKHARI

ABSTRACT

High humidity in room temperature will cause mold formation and contribute to unpleasant odour especially in small places like wardrobe and shoe racks. Moisture absorber is required in order to reduce humidity but the current moisture absorber in the market is costly and utilizes calcium chloride derived from limestone. Limestone mining gave several environmental problems such air pollution and erosion, (Langer, 2011). This project is to discover a greener alternative to producing calcium chloride which using *Anadara granosa* waste. Anadara granosa waste is the cockle shells which abundantly available in Malaysia. This cockle shells has not yet discover the ability to produce moisture absorber medium, calcium chloride. The calcium and carbon content of cockle shell is equivalent to limestone makes it as an alternative to replace limestone as the raw material to produce calcium chloride. This experiment is to synthesis calcium chloride using cockle shell. Calcium chloride is the valuable chemical as moisture absorbent in any dehumidifier product. The experiment product was compared with the commercialize moisture absorber in sorption of moisture capability and the result shows that they are comparable and have the tremendous opportunity to replace limestone as the raw material to produce calcium chloride. As the conclusion, this innovation will able help people to reduce the humidity in a particular disclose area and indirectly can utilize the cockle shell waste.

ACKNOWLEDGEMENT

This project would not have been possible without the assistance and guidance of certain individuals and organization whose contributions have helped in its completion. First of all and most importantly, I would like to express their sincere thanks and utmost appreciation to the lead project supervisor, Dr. Mohd Zamri bin Abdullah for his valuable input and guidance throughout the course of this project.

I would also like to express gratitude to Chemical Engineering Department of Universiti Teknologi PETRONAS (UTP) for providing this chance to undertake this remarkable final year project. A word of sincere gratitude to the Final Year Project committees and lab technician for all the support and knowledge. The seminars were indeed very helpful and insightful. Special thanks to all lecturers from Universiti Teknologi PETRONAS who had provided untiring guidance throughout the period of the project. Last, but certainly not least, I would like to thanks to each individual which very helpful including my friend and all parties that were involved in making this project a success.

TABLE OF CONTENTS

LIST OF FIGURE

LIST OF TABLE

ABBREVIATIONS AND NOMENCLATURES

$CaCO_3$:	Calcium Carbonate
HCl:	Hydrochloric acid
$CaCl_2$:	Calcium chloride
Anadara granosa:	Cockle
$Ca(OH)_2$:	Lime, calcium hydroxide
$Mg(OH)_2$:	Magnesium hydroxide
NaCl:	Sodium chloride

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Malaysia is a country that lies on the equatorial line and has two distinct weather patterns, warm and humid. Throughout the year, Malaysia was recorded with high humidity within 70% to 90%. Having the high humidity condition, it will lead to several problems such as the formation of mold and contribute to unpleasant odour especially in damp and small area. Those enclose area eventually will trap humid from damp shoes or clothes and produce an unpleasant odour. A simpler radiator system maybe can help, but it is not suitable to be used in a small enclosed area like shoe rack or wardrobe. Thus, we need something much cheaper and smaller to dehumidify the humid produce by the damp clothes or shoes.

There are some dehumidifier or moisture absorber products that are available in the market nowadays. However, those products are expensive and using the limestone as main raw material. Problem of limestone is the mining activities at quarries and depleting resource. Mining activities contribute environmental impact such as blasting activity impact, dust, water quality, noise and others (Langer, 2011). The mining large quantities of raw materials result in extensive deforestation and top soil loss (Mehta, 2001). So we need to come out with a green product that is using waste materials. So, this study will be done to study on the sorption of moisture by the *Anadara granosa* waste. This study is an experimental study to produce calcium chloride as a moisture absorber medium from *Anadara granosa* waste. *Anadara granosa* is also known as blood cockle or 'kerang' for Malaysian community. The calcium chloride is one of the compounds which act as moisture absorber. The project will cover the composition of calcium carbonate in the cockle shell and ability of the produced calcium chloride to absorb moisture. The purpose of research is to find the yield percentage of calcium chloride from reaction of *Anadara granosa* waste with hydrochloride acid and the performance of the calcium chloride produced as moisture absorber. The experiment will conduct using different concentration of hydrochloric acid to produce calcium chloride. The existing dehumidifier's adsorbent is either made from chemical or not environmental friendly. These biological resources such as limestone and calcite are depleting.

1.2 Problem Statement

In the enclosed areas such as cupboard and wardrobe, the presence of moisture subjected to humidity causes the formation of mildew and mold that is not only affected the user's health and safety due to inhalation, but also damages properties. A way to reduce humidity is to use dehumidifier in a form of small container consisting of moisture absorber in the said area. The moisture absorber in the market nowadays is expensive and most of them are using calcium carbonate. Current technology in supplying calcium carbonate is through the mining activities at the quarries, by which despite the continual supply of the raw material, the activity has tremendously depleted the quality of the environment. One example is at Simpang Pulai area in Perak, where the mining activities has caused erosion to the hills, reduce the air quality and polluted the area. Greener technology should be develop in reduce the impact of mining activities to the environment.

1.3 Objectives and Scope of Study

1.3.1 Objective

The aim of the project is to study the sorption of moisture by the *Anadara granosa* waste. This project will cover the following objectives:

1) To study on the percentage of yield of calcium chloride synthesized from waste cockle shells.
2) To study on the moisture sorption capacity of the calcium chloride produced from waste cockle shell.

1.3.2 Scope of Study

The project involves experimental work by which waste cockle shells will be sourced from the local supply and undergone a series of preparation methods. The shells will then be subjected to the reaction with acidic medium at various concentrations to produce calcium chloride, i.e. the active chemical for the moisture sorption. The capacity to absorb moisture will be further investigated in a controlled environment to determine its effectiveness.

CHAPTER 2

LITERATURE REVIEW

2.1 Anadara granosa and Sustainability

Anadara granosa is a type of cockle well known as 'kerang' among the Malaysian locals. Natural distribution of cockle is confined to the coastal region of Peninsular Malaysia, particularly in Malacca and Selangor. The habitat of the cockle is in the large estuarine mudflats bordered landward by mangroves. Cockle is a famous delicacy and easily obtained in the country all year round. 80% of total weight of cockle is the cockle shell; only 20% are used as protein food. Because of that condition, the *Anadara granosa* waste contributes 80% of the total cockle produced. Cockle shell, which is available in abundance, It has no any eminent use and is commonly regarded as a waste.

Figure 1: *Anadara granosa* or Cockle

Fully utilize the *Anadara granosa* waste to synthesis calcium carbonate will decrease the unused waste capacity. Apart from that, the process is a simple, low-cost, and environmentally friendly method for the synthesis of calcium carbonate from a low-cost and abundant natural resource, cockle shells.

As an alternative to extraction of $CaCO_3$ through mining, cockle shells are identified to be the potential biomass source. The selection of cockle shell is based on the fact that cockle shells contain of 95-99% by weight of $CaCO_3$ (Nakatani et al, 2009). In addition to that, realizing the fact that cockle is commonly used for protein source food, government of Malaysia has put much emphasis on its production. In the ninth Malaysian plan, the expected production of cockle shell is estimated to be around 1300 metric ton (2007). Up until 2007, the total area involved in the cockle cultivation agriculture is estimated to be 6000 hectare involving some 1055 farmers. This large number not only reflects the huge amount of cockle shells produced but also images the amount of waste shell generated. Dumping shells untreated can produce unpleasant odor as well as distressing the view of the surrounding. In 2009, the total cockle were produced around 65000 metric tons (FISHMAIL,2011).

2.2 *Anadara granosa* Waste Study and Application

Mohammad et al (2010) did a research on the characterizing the cockle shell to produce bioceramic. The research was using X-ray fluorescence, spectroscopy, porosity and density analysis and compression test. Following table is from the research. More than 98% of the cockle shell was containing calcium element in form of calcium oxide. The other component is including the trace element in the cockle shell.

Table 1: The Mineral Composition of Pure *Anadara granosa* (Pure Ag), HAP-Ag, Bioceramic Compared to Synthetic HAP [Mohammad, N.F et al, 2010]

Minerals	Concentration (%)		
	pure-Ag	HAP-Ag	HAP
Al_2O_3	0.25	0.3	-
CaO	98.11	83.97	57.86
TiO_2	0.13	-	0.005
V_2O_5	0.062	-	-
Cr_2O_3	0.04	-	0.02
MnO	0.022	0.028	0.01
Fe_2O_3	0.503	0.083	0.034
CuO	0.034	0.053	0.02
SrO	0.402	0.51	0.025
RuO_2	0.43	0.69	
LuO_3	0.009	0.01	0.008
P_2O_5	-	14.2	41.9
Er_2O_3	-	0.10	-
BaO			0.075
La_2O_3			0.04

Awang-Hazmi et al, (2007) made a conclusion from their research that the percentage of CaC composition is more than 98.7% of the total minerals content of the cockle shells. About 1.3 % of the composition are comprises of Mg, Na, P, K and others (Fe, Cu, Ni, B, Zn and Si).Overall, the minerals composition of cockle shells of West Coast of Peninsular Malaysia are as followed: CaC 98.7 %, Mg 0.05%, Na 0.9%, p 0.02 and others 0.2%. The table following is according to the location cockle shell origin.

Table 2: Percentage of major mineral contents of cockle shells [Awang-Hazmi, A.J et al, 2007]

Sources/Minerals	Ca+C	Mg	Na	P	K	Others
Penang	98.770	0.0476	0.9192	0.0183	0.0398	0.1981
Kuala Selangor	98.8007	0.0477	0.9076	0.0176	0.0392	0.1871
Malacca	98.7834	0.0437	0.9386	0.0178	0.0380	0.1894

Barros et al, (2009) also specify the composition of the calcium chloride in the mussel shell is more than 95% from the total mineral content. Another research was done to synthesis the calcium carbonate nanocrystal. On the basis of the analysis of calcium carbonate nanocrystals from the cockle shell powder and that of the powder itself, the shells are composed of the aragonite form of calcium carbonate, which is less stable and denser than calcite. According to Ibrahim, (1994) there are 17 different trace element in cockle shell including As, Br,Cs,Eu,Ce,Lu,Tb and Yb. The experiment was using the technique of instrumental neutron activation analysis (INAA).

Table 3: Application of Seashells in other Countries (*Mohamed et al., 2012*)

Type of Seashell	**Country**	**Application**
Oysters	Japan	Cement clinkers
	Korea	Fertilizers, water eutrophication
Scallops	UK	Construction road forestry
	Peru	Obtain lime as the input for other industrial sector
Mussels	Spain	Animal feed additives, liming agent, constituent
	US	Fertilizers
	Holland	Soil conditioner, liming agent
		Mussel tiles

Peng-Lim et al,(2011) was using anadara granosa waste as the source of calcium oxide in producing biodiesel. Calcium oxide is very important in catalyzing a transesterification reaction in producing biodiesel (methyl ester). In material preparation, the shells were cleaned by washing thoroughly with warm water several times. Then they were dried overnight in an oven at 105 C. Crushed and powdered shells were then sieved (<1 mm) before being subjected to the experiment.

Other studies on the cockle shell were summaries in following table:

Table 4: Cockle shell studies and application

Study	Application	Researcher
Construction material	Alternative Construction Material For Artificial Reef	Sahari et al
Mineral and Physichochemical Characterization	Biomaterial for Bone Tissue Engineering.	Awang-Azmi et al,(2008)
A Study of Calcination and Carbonation	Calcium Oxide	Rashidi et al
Develop new source for cement production	Cement product for masonry and plastering	Lertwattanaruk et al (2012)

From all the studies and the application has not yet involving the use of cockle shell as the main source to produce calcium chloride as moisture absorber. This project is still in early stage to determine the potential of production calcium chloride from cockle shell waste. A good potential on this project due to the calcium and carbon content of cockle shell which comparable with the limestone. This approach will lead to a great greener technology which utilize the waste and reduce the mining effect on the environment.

2.3 Calcium Chloride as Moisture Absorber

In 1960, a research on calcium chloride already discover as a good moisture absorber component. Calcium chloride was able to prevent the increasing of humidity in packaging the fresh fruit and vegetables (Eaves, 1960). The other well-known moisture absorbers are sorbitol, xylitol, montmorillonite clay and silica. From the moisture absorbers element, calcium chloride is always on the top. In other research, Irfan et al (2013) was focus on the ability of calcium chloride in expands the quality of fig fruit during storage. The result from the research was show that the existing of 4% calcium chloride in the storage at 1+/- 0.5°C with 95-98% relative humidity already big enough to keep the fig fruit for 14 days.

Different moisture absorber elements or desiccants are widely known in industries application can be summaries in the following table:

Table 5: Different of moisture absorbent available in industries

Absorbent	Synthesis	Moisture adsorptive capacity	Price
Montmorillonite Clay	Naturally occurring adsorbent created by the controlled drying of magnesium aluminum silicate of the sub-bentonite type.	Highly effective within normal temperature and relative humidity ranges. Not effective in excess moisture content.	Cheap
Silica Gel	Naturally occurring mineral that is purified and processed into either granular or beaded form.	Silica gel performs best at room temperatures (70° to 90°F) and high humidity (60 to 90% RH) and will drop the relative humidity in a container down to around 40% RH.	Expensive
Indicating Silica Gel	Silica gel bead or granule that has been washed with a concentration of cobalt chloride.	Color changes as the desiccant goes past 8% moisture levels (by weight) and indicates it is time to replace the desiccant.	Expensive
Molecular Sieve	Synthetic porous crystalline aluminosilicates which have been engineered to have a very strong affinity for specifically sized molecules.	Molecular sieve can trap water vapor to temperatures well past 225°C in some cases, and due to its high affinity for water vapor, molecular sieve is able to bring the relative humidity (RH) in environments down to as low as 1% RH.	Very expensive
Calcium Oxide	Calcinated or recalcinated lime	Not less than 28.5% by weight.	Expensive
Calcium Sulfate	Created by the controlled dehydration of gypsum	Adsorb only up to 10% of its weight in water vapor.	Expensive
Calcium Chloride	Salt of calcium and chloride	Strong moisture-sorption property works great in variety of surrounding conditions	Expensive

Silica-based compound is not used due to its high toxicity, while clay lack in the effectiveness in absorbing excess moisture. This left calcium chloride as the best choice as its strong moisture-sorption property works great in variety of surrounding conditions. Some of the well-known moisture absorbers in the market such as Thirsty Hippo, DampRid, and Dessicare, use calcium chloride as the moisture-sorbing chemical.

Weatherly Japan K.K. is also choosing calcium chloride as the best moisture absorbent. From the article, they made a comparison with calcium chloride with silica gel.

Table 6: Calcium chloride and silica gel comparison [Weatherly Japan K.K]

Comparison	Calcium Chloride	Silica Gel
Absorption Capacity Desiccant materials absorb greater amounts of moisture when the relative humidity of the surrounding air is higher.	150% At a relative humidity (RH) of only 50%, calcium chloride's moisture absorption is 150% its weight in water. Its absorption increases exponentially as RH rises, to 600% at 85%RH.	25% Silica gel absorbs poorly at low RH, trapping only 25% of its weight at 50% humidity. Unlike calcium chloride's exponential curve, silica gel's absorption is more linear—only 36% at 85%RH.
Safe Against Exhaustion Some absorbers can exhaust themselves before the voyage has completed, due to temporary humidity spikes	Yes Calcium chloride is self-limiting, allowing it to continue protecting for long periods without running itself out during short periods of high RH. Spikes are dampened but without saturating the desiccant.	No Silica gel absorbs water into microscopic pores. If a short spike in humidity is encountered early in the voyage, all pores can physically saturate, leaving cargo unprotected.
Environmentally Safe Many absorption materials contain moisture indicator additives that are classified as toxic.	Yes Calcium chloride, a kind of salt compound Non-toxic, it can be disposed with regular wastewater.	No Many silica gels contain cobalt compounds that are considered carcinogenic and require special disposal using hazardous waste procedures.

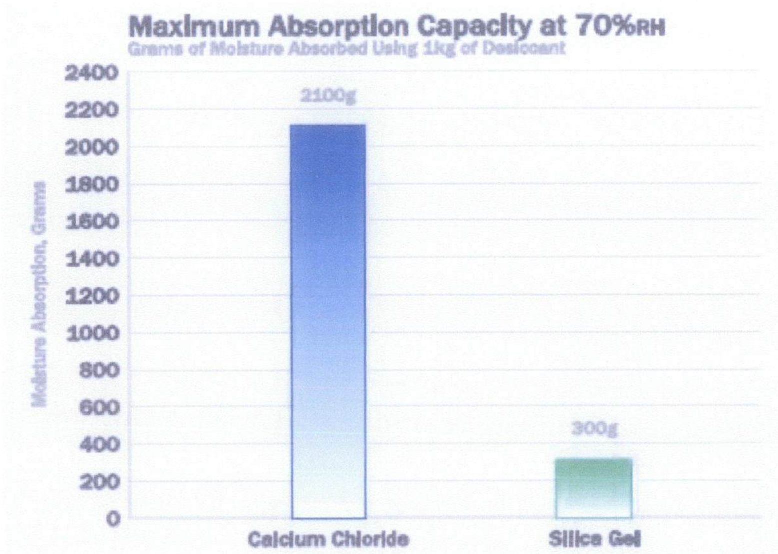


Figure 2: The maximum absorption capacity at 70% relative humidity, (Weatherly Japan K.K)

The calcium chloride can perform seven times better than silica gel with various advantages over it. From these study, research and article, calcium chloride has a good perspective in moisture absorption as the absorbent. It makes this product is very valuable and has high demand with a good specification in sorption of moisture.

2.4 Use of moisture absorber

Moisture absorber is the most important medium to keep a good condition of an asset especially for asset that effected due to moisture content or water vapor. A good moisture absorber will absorb any moisture in that area to avoid the damage on the asset and prevent any mildew formation or bad adour in that space area. The following table 7 was summaries the use of moisture absorber in different application.

Table 7: Uses of moisture absorber

Application	Description
Electronics	Avoid damage to non water proof electronic stuff
Food	Needs it to stay clean and dry when stored.
Shipping	Keep that cargo safe in damp condition.
Tools	Keep their metal rust-free and their wood strong.
Laboratory	Keep the laboratory equipment in good condition
Personal Use	Prevent mildew, and bad odor in cupboard

2.5 Calcium chloride synthesis

The reaction to produce calcium chloride from calcium carbonate is such follow:

$$2HCl(aq) + CaCO_3(s) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

The reaction of calcium carbonate with hydrochloric acid is said to be **first order** with respect to hydrochloric acid. This is because the rate depends upon the concentration of hydrochloric acid to the power one. The rate of reaction can be determine using the amount of reactant change which calcium carbonate and hydrochloric acid or the product form which, calcium chloride, water and carbon dioxide. This reaction is irreversible reaction which allowing the physical drying of the solution to obtain solid form of calcium chloride.

The conventional way to produce calcium chloride is using limestone-hydrochloride acid process and natural brine process. The Natural Brine Process is a process that has been discovered in U.S by using salt lakes and salt deposits. The process is utilized by the concentration and purification of naturally occurring brines. Magnesium is removed by adding milk of lime, $Ca(OH)_2$, which causes magnesium to precipitate in the form of magnesium hydroxide, $Mg(OH)_2$. Sodium chloride, NaCl, is removed by precipitation; sodium chloride precipitates from the $CaCl_2$ solution when the concentration of calcium chloride is increased during the evaporation of water.

$$Ca(OH)_2 + Mg^{2+} \rightarrow Mg(OH)_2 + Ca^{2+}$$

The advantage of this source of calcium chloride is the low raw material cost and low environmental impact. However, the purity of the product is normally lower than the competing processes.

In Limestone-Hydrochloric Acid Process, limestone can be treated with hydrochloric acid to form calcium chloride and carbon dioxide:

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$$

This process is most favorable method in the process producing calcium chloride due to high composition value of calcium carbonate which leads to good calcium chloride product. From the conventional way, limestone with 36% concentrated hydrochloride acid was able to produce 40% concentrated calcium chloride solution.

Composition of component in limestone in Malaysia is such below:

Table 8: Composition of Mineral from Thang Kiang Nam Quarry Limestone Specification

Thang Kiang Nam Quarry Limestone Specification	
CaO	55.0%
*equivalent $CaCO_3$	98.2%
MgO	0.65%
*equivalent $MgCO_3$	1.36%
Acid Insoluble	0.07%
SiO_2	0.01%
Fe_2O_3	0.03%
*Al_2O_3	0.04%
*LOI	42.5%

The process of drying is required in order to obtain the solid form of calcium chloride. Since this synthesis is irreversible process, physical drying can be perform which required heating medium to evaporate the water from the concentrated solution of calcium chloride

From the above research from Barros et al (2009), Awang-Hazmi et al, (2007), Mohammad et al ,(2010) and Nakatani et al, (2009), cockle shell has a great composition of calcium carbonate which is more than 95%. Compared to the conventional way of producing calcium carbonate from mining at the quarries, the composition of calcium carbonate is more or less the same. It would be better to use cockle shell as the main calcium carbonate source. This will bring large benefits to the environment rather than using limestone. Besides that, fully utilization of the cockle shells will promote the greener technology and decrease the unused waste capacity. Rate of reaction are varies with the concentration of the reactant.

CHAPTER 3

METHODOLOGY

3.1 Research Methodologies

This project refers to following flow of methodology to fulfill the mentioned objectives.

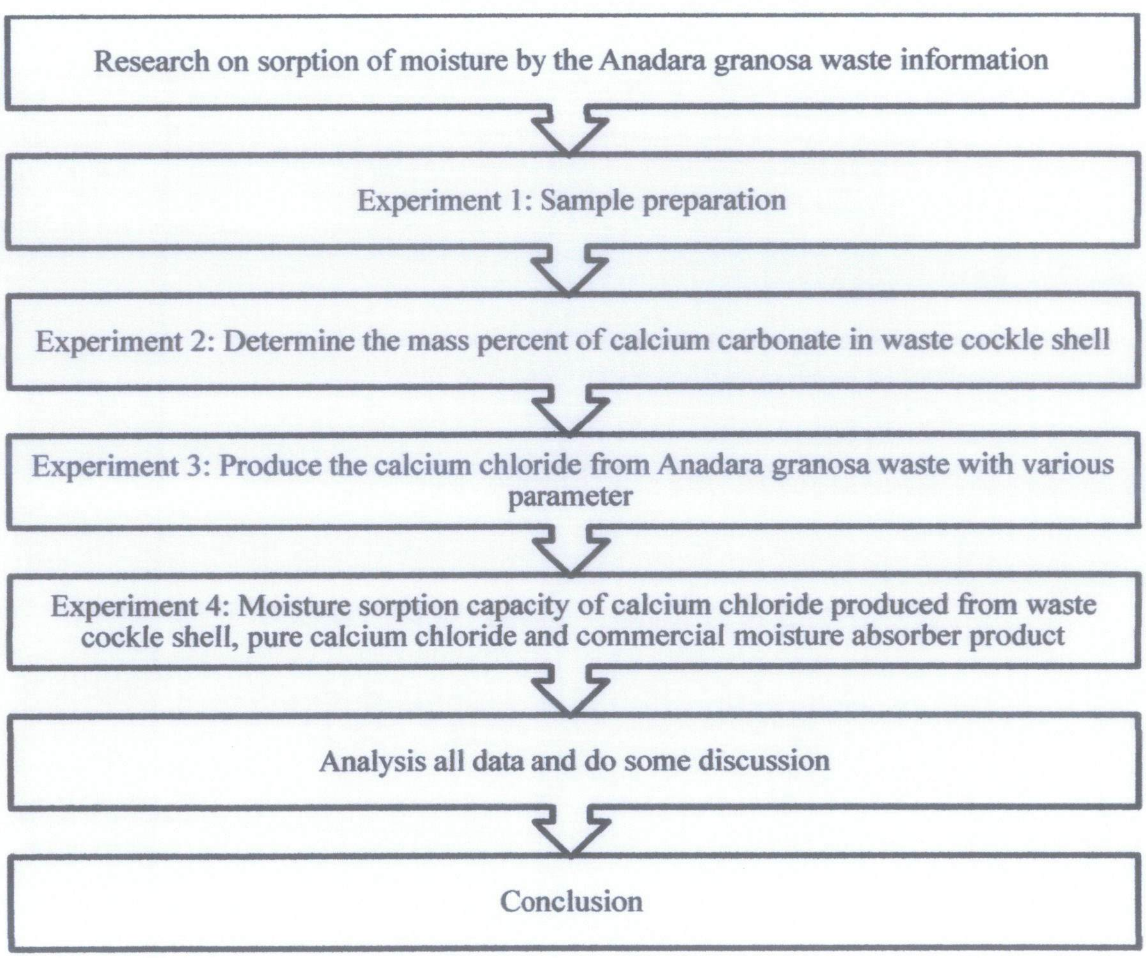


Figure 3: Methodology for sorption of moisture by the *Anadara granosa* waste

3.2 Procedure of experiment

3.2.1 Experiment 1: Sample preparation

The sample preparation is needed to prepare sample for next experiment and to remove any impurities in the sample.

i. The cockle shell is washed with distilled water until all traces of dirt and dust were removed.
ii. They are dried in an oven at 110 °C for 2 hours.
iii. The cockle shell is then crushed and grounded into fine powder by Rocklabs rotation grinder. Size of particle is 0.5 mm to 3.0 mm.
iv. The size of particle then separate in 3 beakers according to its size.

3.2.2 Experiment 2: Determination of the mass percent of calcium carbonate in waste cockle shell

The cockle shells are mostly consisted of calcium carbonate but not at 100% purity. The following steps will investigate the percentage of calcium carbonate in cockle shell in mass basis:

i. 5M of HCl and 0.1M of NaOH was prepared accordingly.
ii. 10ml of 5M of hydrochloric acid was measured.
iii. 2g of 0.5 mm particle size of cockle shell was weighed.
iv. Place the beaker with hydrochloric acid in the water bath basin.
v. Mix the cockle shell and hydrochloric acid.
vi. The solution was stirred until the reaction complete (note: The reaction was producing carbon dioxide which forming bubble, reaction is complete whenever no bubble formed)
vii. The mixture then filtered into a conical flask to separate the impurities, and any residue which left the calcium chloride, water and unconverted hydrochloric acid.
viii. A few drop of phenolphthalein was added into the conical flask then the solution was titrated with 0.1M sodium hydroxide until the solution change color.
ix. The experiment was repeated for 3mm and granule form of cockle shell.

x. The mass of calcium carbonate was estimated using following figure.

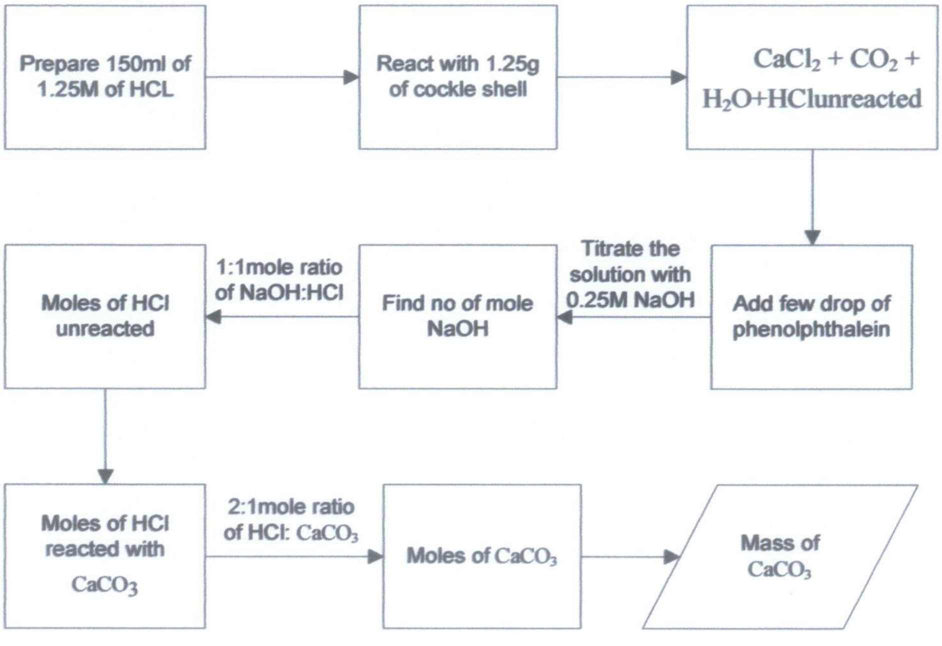
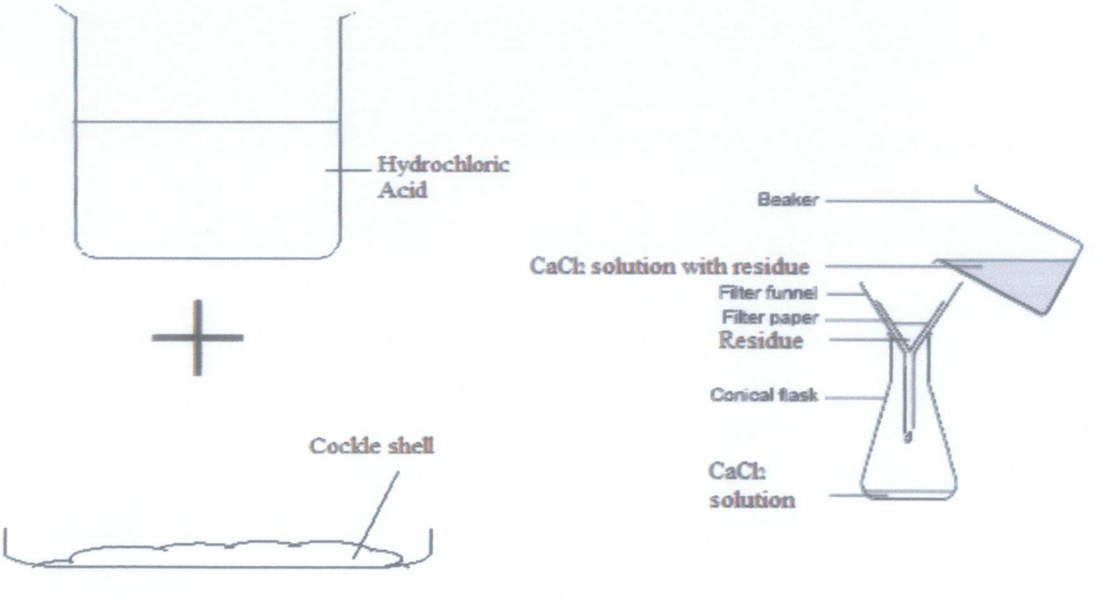


Figure 4: Mass percentage $CaCO_3$ in cockle shell procedure



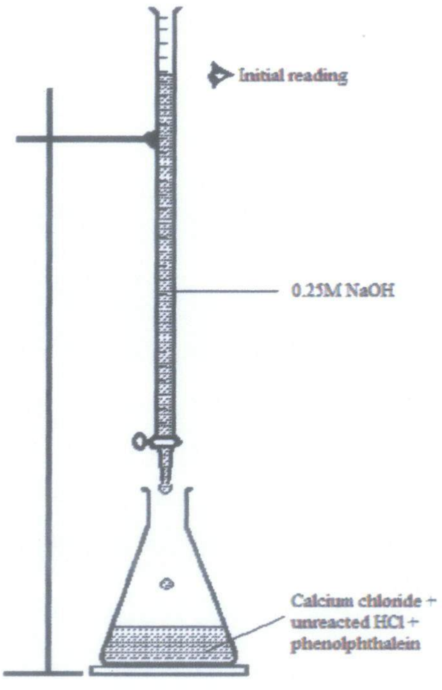


Figure 5: Experiment setup for mass percentage $CaCO_3$ in cockle shell procedure

3.2.3 Experiment 3: Produce the calcium chloride from Anadara granosa waste with various parameter

i. Concentration of hydrochloric acid

The experiment is carried out using the powder form of cockle shell waste which obtains from sample preparation. In order to have the same size of the prepared sample, a sieve shaker is used. The experiment is carried out in controlled environment. Following is the procedure of this experiment:

1. 1M of HCl was prepared accordingly..
2. 100ml of 1M of HCl was measured and pour it to beaker.
3. 25g of 0.5 mm particle size of cockle shell was weighed.
4. The beaker with HCl was placed in the water bath basin.
5. Then, cockle shell was mixed into 1M of HCl and starts the stopwatch.

6. The solution was stirred until the reaction complete (note: The reaction will produce carbon dioxide which forming bubble, reaction is complete whenever no bubble formed)

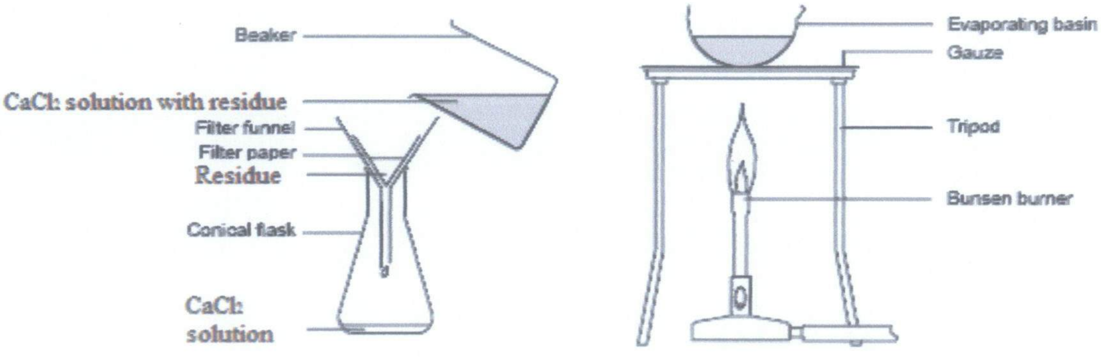


Figure 6: Experiment 3 setup

7. The mixture then filtered into a conical flask to separate the impurities, unconverted reactant and any residue which left the calcium chloride solution.
8. The filtrate then transferred into evaporating basin.
9. In order to obtain the solid form of calcium chloride, the solution was heated gently until it starts to decrepitate and further drying in oven with 100°C.
10. The dried calcium chloride was weighed and recorded.
11. The experiment was repeated twice to obtain the average value.
12. The experiment then repeated for 3M, 5M and 7M of HCl.

ii. Size of waste cockle shell

The experiment is carried out to determine the effect of size of the sample in producing the calcium chloride. The procedure is such below:

1. 25g of 3 mm particle size of cockle shell was weighed to be use in this experiment.
2. Using the same experimental procedure and setup, the experiment was conducted using 25g of 3 mm particle size to replace the powdered sample, 0.5 mm particle size.
3. The experiment was repeated twice to obtain the average value.
4. The experiment then repeated for granule size of cockle shell

3.2.4 Experiment 4: Moisture sorption capacity of calcium chloride produced from waste cockle shell, pure calcium chloride and commercial moisture absorber product

The experiment is using 3 type of moisture absorber which the pure calcium chloride, the best yield of calcium chloride produced from experiment 3 and commercial moisture absorber product. The procedure of this experiment is such below:

1. 4g of pure calcium chloride was weighed and placed in a beaker.
2. 100 ml of water was measured and poured it into a beaker.
3. The experiment was conducted as follow:

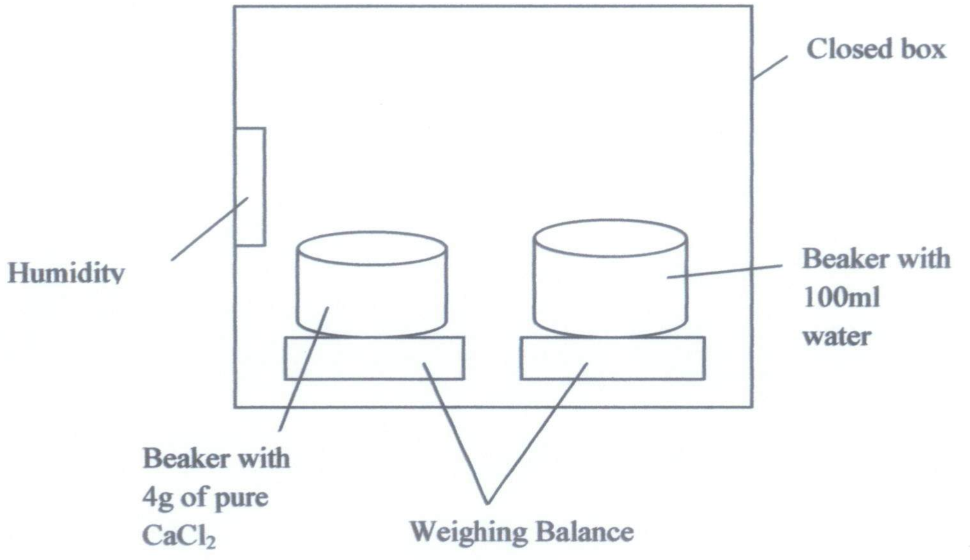


Figure 7: Experiment 4 setup

4. The humidity and temperature was recorded.
5. The initial weigh of beaker containing 4 g of pure $CaCl_2$ and beaker containing 100ml water was recorded and the reading for every 24 hours was recorded for 15 days.
6. The experiment was repeated using calcium chloride produced from experiment 3 and commercial moisture absorber product to replace pure calcium chloride.

Time (d)	Weight of water (g)		
	Pure calcium chloride	Produced calcium chloride	Commercial Moisture absorber
1			
2			
•			
•			
•			
15			

3.3 Gantt Chart and Key Milestone

No.	Detail Work	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28
1	Topic Selection																												
2	Information Research																												
3	Proposal Defence																												
4	Design Experiment Set-up																												
5	Purchase Additional Equipment and Chemical																												
6	Interim Report																												
7	Experiment 1																												
8	Experiment 2																												
9	Experiment 3																												
10	Experiment 4																												
11	Data Analysis and Discussion																												
12	Conclusion																												
14	Final report																												

Table 9: Gantt Chart and Key Milestone

3.4 Project Activities

This project will be involved in experimental work. Following is the list of experimental for this project.

- Experiment 1: Sample preparation
- Experiment 2: Determine the mass percent of calcium carbonate in waste cockle shell
- Experiment 3: Produce the calcium chloride from Anadara granosa waste with various parameter
- Experiment 4: Moisture sorption capacity of calcium chloride produced from waste cockle shell, pure calcium chloride and commercial moisture absorber product

3.5 Tools, Equipment and Material

- **Chemical and raw material**
  a. Cockle shell
  b. Hydrochloric acid
  c. Pure calcium chloride
  d. Sodium hydroxide
  e. Commercial dehumidifier products
- **Equipment**
  a. Oven
  b. Grinder
  c. Experiment apparatus
  d. Humidity meter

CHAPTER 4

RESULT AND DISCUSSION

4.1 Experiment 1:

Sample preparation

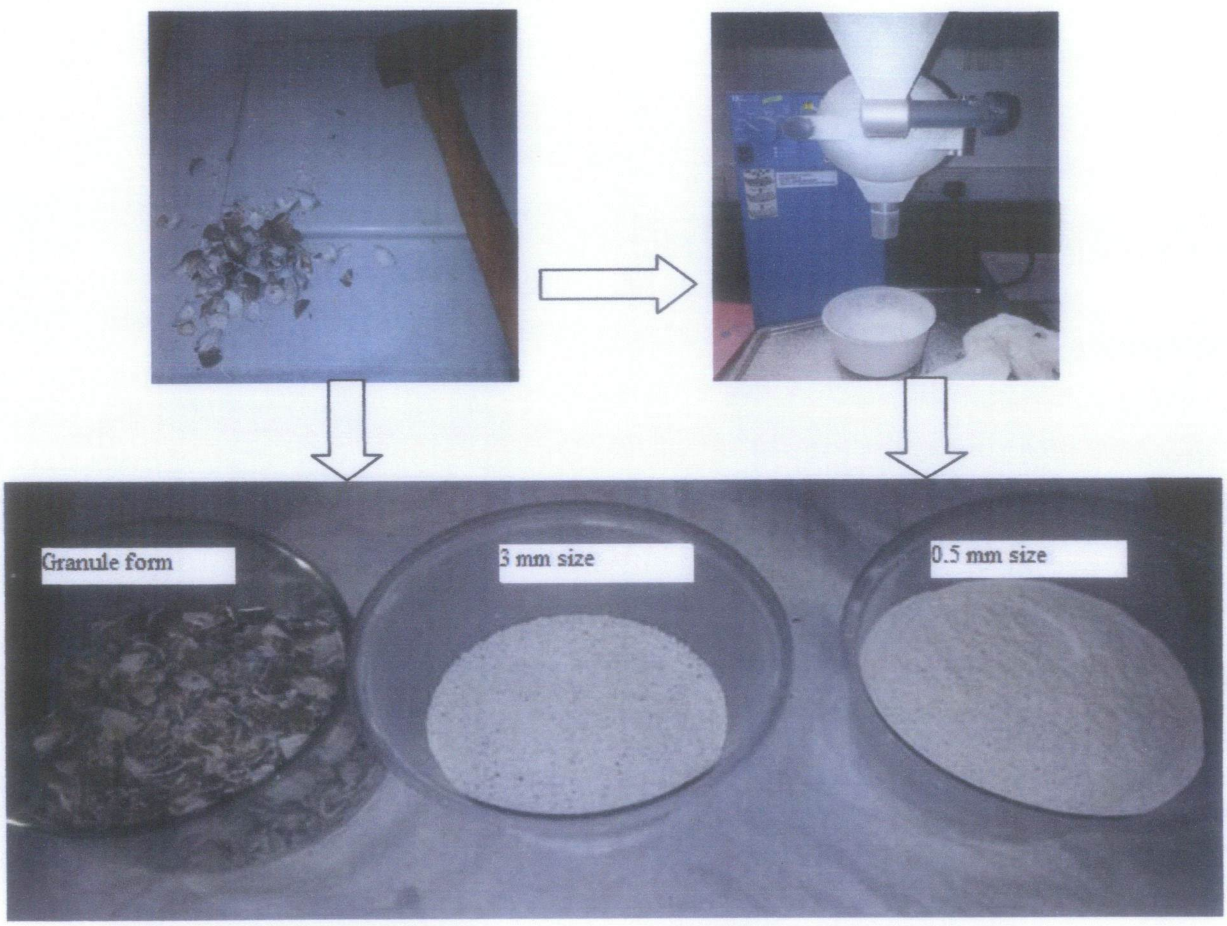


Figure 8: Different size cockle shell particle

4.2 Experiment 2:

Determine the mass percent of calcium carbonate in cockle shell

The experiment was successfully in finding the mass percent of $CaCO_3$ in cockle shell by gravimetric analysis. The result of this experiment was based on the following calculation.

$$\text{Mass percent of } CaCO_3 \text{ in cockle shell} = \frac{mass\ of\ CaCO_3}{mass\ of\ cockle\ shell} \times 100$$

$$\underset{\text{(in excess)}}{2HCl(aq)} + \underset{\text{(limiting reagent)}}{CaCO_3(s)} \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l) + \underset{\text{(unreacted)}}{HCl(aq)} \qquad (1)$$

$$\underset{\text{(unreacted)}}{HCl(aq)} + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l) \qquad (2)$$

Initial moles of HCl	0.0375mole
Average volume of NaOH	56ml
Mole of NaOH=0.056L(0.25M)	0.014mol
Mole of unreacted HCL= moles of NaOH	0.014mol
Mole of reacted HCl	0.0375-0.014=0.0235mol
Mole of reacted CaCO3	0.0235/2=0.01175mol
Mass of CaCO3=0.01175mol(100.09g/mol)	1.176g

$$\text{Mass percent of } CaCO_3 \text{ in cockle shell} = \frac{mass\ of\ CaCO_3}{mass\ of\ cockle\ shell} \times 100$$

$$= \frac{1.176}{1.25} \times 100 = 94\%$$

From the calculation mass of calcium carbonate in cockle shell, it gives 94 mass% of cockle shell is calcium carbonate. The other 6% is the trace element the impurities and the dirt of the cockle shell. This experiment was proven that the $CaCO_3$ is the main component in cockle shell.

4.3 Experiment 3:

Calcium chloride synthesized from *anadara granosa* waste with various parameters

This experiment was done for two different parameters, which is concentration of HCl and size of cockle shell. The outcome of this experiment is to determine the actual yield from the reaction, rate of reaction, and percentage yield for all trials. The best yield then will be used in experiment 4 for the moisture sorption capacity performance.

Figure 9: The $CaCl_2$ product from reacting HCl and cockle shell.

The result was tabulated in following tables according to different size of cockle shell and concentration of HCl. The results consist of actual yield, time for complete reaction, theoretical yield and percent yield.

Table 10: Percent yield of $CaCl_2$ for 3 different sizes using 1M of HCl.

Size of cockle shell	$CaCl_2$ produced (actual yield) (g)	Time to complete reaction (mins)	Theoretical yield (g)	Percent yield	Mass $CaCl_2$ produced/ Mass of cockle shell
0.5 mm	4.21	40	5.55	75.80	0.17
3 mm	4.12	75	5.55	74.25	0.16
granule	4.06	125	5.55	73.15	0.16

Table 11: Percent yield of $CaCl_2$ for 3 different sizes using 3M of HCl

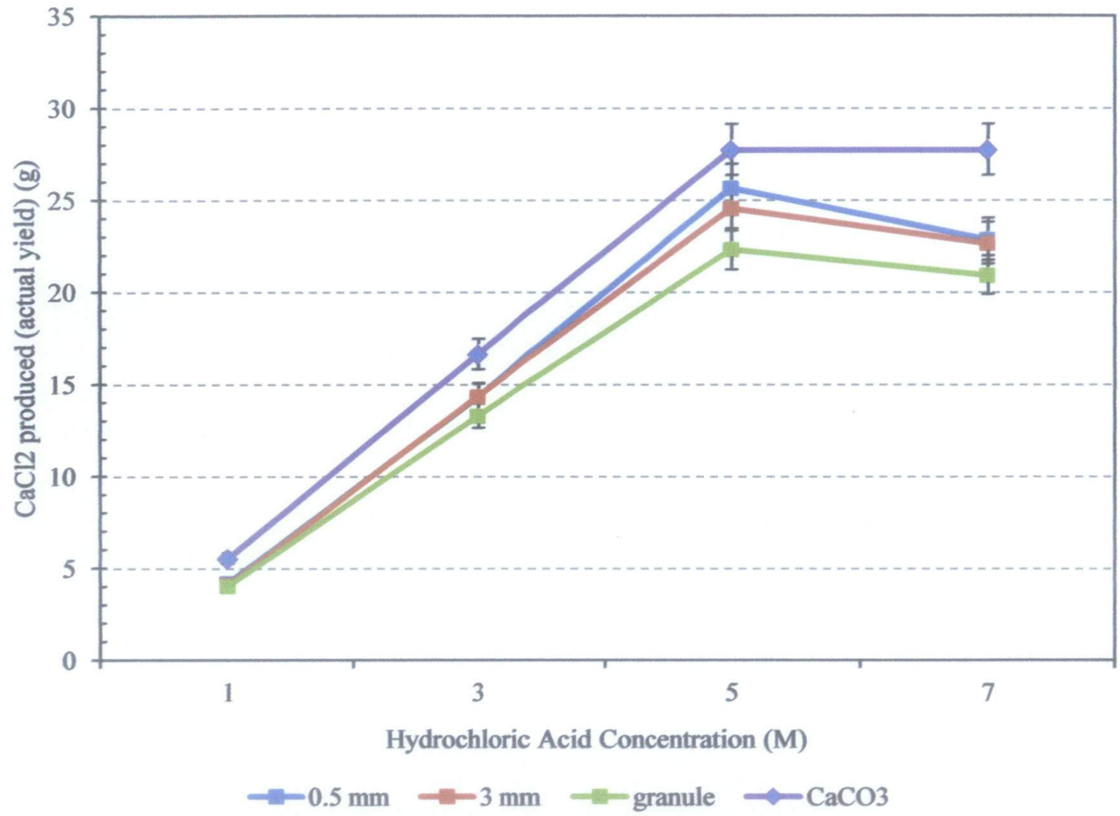
Size of cockle shell	$CaCl_2$ produced (actual yield) (g)	Time to complete reaction (mins)	Theoretical yield (g)	Percent yield	Mass $CaCl_2$ produced/ Mass of cockle shell
0.5 mm	14.33	32	16.65	86.06	0.57
3 mm	14.35	60	16.65	86.20	0.57
granule	13.29	100	16.65	79.85	0.53

Table 12: Percent yield of $CaCl_2$ for 3 different sizes using 5M of HCl.

Size of cockle shell	$CaCl_2$ produced (actual yield) (g)	Time to complete reaction (mins)	Theoretical yield (g)	Percent yield	Mass $CaCl_2$ produced/ Mass of cockle shell
0.5 mm	25.68	23	27.74	92.55	1.03
3 mm	24.57	33	27.74	88.55	0.98
granule	22.34	68	27.74	80.52	0.89

Table 13: Percent yield of $CaCl_2$ for 3 different sizes using 7M of HCl.

Size of cockle shell	$CaCl_2$ produced (actual yield) (g)	Time to complete reaction (mins)	Theoretical yield (g)	Percent yield	Mass $CaCl_2$ produced/ Mass of cockle shell
0.5 mm	22.88	8	27.74	82.46	0.92
3 mm	22.68	10	27.74	81.73	0.91
granule	20.94	20	27.74	75.46	0.84



Note: The $CaCO_3$ is the reference maximum point of calcium chloride production.

Figure 10: The actual yield of calcium chloride using different concentration of HCl for different size of cockle shell.

Calcium chloride produced was indicating the actual yield of the reaction and all its value is the average for three trials for each sub experiment. From the result obtained, the highest yield is 25.678g from combination of 0.5mm size of cockle shell and 5M of HCl. The increasing of molarity of HCl will increase the yield of $CaCl_2$ but the yield of $CaCl_2$ begin to decrease for molarity of HCl more than 5M. The optimum value HCl molarity is 5M. The production of $CaCl_2$ was decrease after 5M of HCl due to the impurities limitation of cockle shell. The possible impurities was involve in the reaction is magnesium content in cockle shell. The calcium carbonate ($CaCO_3$) was the indication of cockle shell with 100% purity of cockle shell which in the result shows that the maximum production of cockle shell will not exceed the 100% purity $CaCO_3$.

This result also proves that the purity of cockle shell is below than 100% purity of $CaCO_3$.

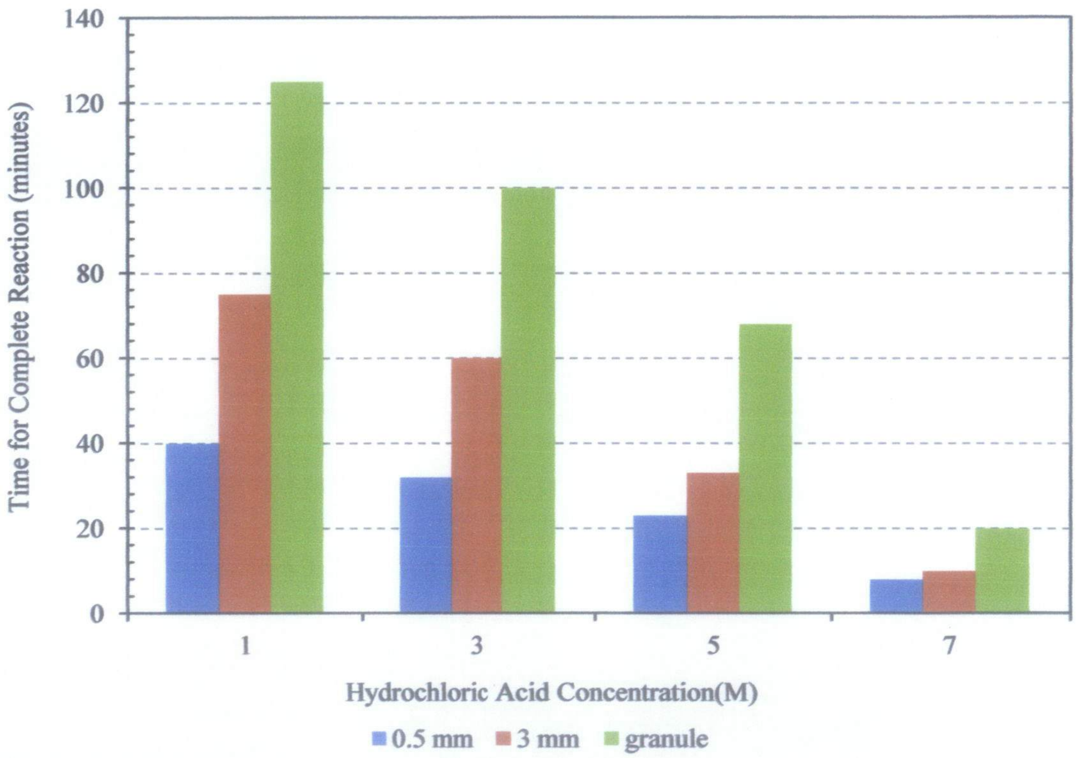


Figure 11: The reaction time for different concentration of HCl with different size of cockle shell.

The fastest reaction was determined for smallest size of cockle shell which 0.5mm for every trial compared to 3mm and granule form of cockle shell size. The reaction is faster for small size of particle because the surface area is larger than the bigger size of particle. A larger surface area is a much easy target for colliding molecules. The bigger the target, the easier it is to hit. Fine powders therefore react faster than coarse powders and granule form. Since the reaction rate is depend on the concentration of HCl, the reaction time was varies with different concentration. The fastest reaction time was observed for 7M of HCl. Increasing the concentration of HCl, the reaction time will decrease.

Theoretical yield is estimate with assuming the cockle shell is having 100% purity of calcium carbonate through following calculation:

Theoretical yield calculation:

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$$

Identify the limiting reactant and calculate the $CaCl_2$ produced.

Table 14: Theoretical yield calculation.

Molarity HCl	Limiting reactant	$CaCl_2$ theoretical yield
1M	HCl =0.1 mol	0.1 mol HCl will produce 0.05 mole $CaCl_2$ $0.05 \text{ mol } CaCl_2 \times \frac{110.98\text{g } CaCl_2}{1 \text{ mol } CaCl_2} = 5.549\text{g } CaCl_2$
3M	HCl = 0.3mol	0.3 mol HCl will produce 0.15 mole $CaCl_2$ $0.15 \text{ mol } CaCl_2 \times \frac{110.98\text{g } CaCl_2}{1 \text{ mol } CaCl_2} = 16.647\text{g } CaCl_2$
5M	$CaCO_3$=0.25 mol	0.25 mol $CaCO_3$ will produce 0.25 mole $CaCl_2$ $0.25 \text{ mol } CaCl_2 \times \frac{110.98\text{g } CaCl_2}{1 \text{ mol } CaCl_2} = 27.745\text{g } CaCl_2$
7M	$CaCO_3$=0.25 mol	0.25 mol $CaCO_3$ will produce 0.25 mole $CaCl_2$ $0.25 \text{ mol } CaCl_2 \times \frac{110.98\text{g } CaCl_2}{1 \text{ mol } CaCl_2} = 27.745\text{g } CaCl_2$

Percent yield of $CaCl_2$ was calculated with following formula:

$$CaCl_2 \text{percent yield} = \frac{CaCl_2 \text{ actual yield}}{CaCl_2 \text{ theoretical yield}} \times 100$$

Percent yield of $CaCl_2$ was indicated the percentage of actual yield by experimental value to theoretical yield by mathematical calculation base on complete reaction basis. From the result obtained, the best percent yield is 92.55% from combination of 0.5mm size of cockle shell and 5M of HCl.

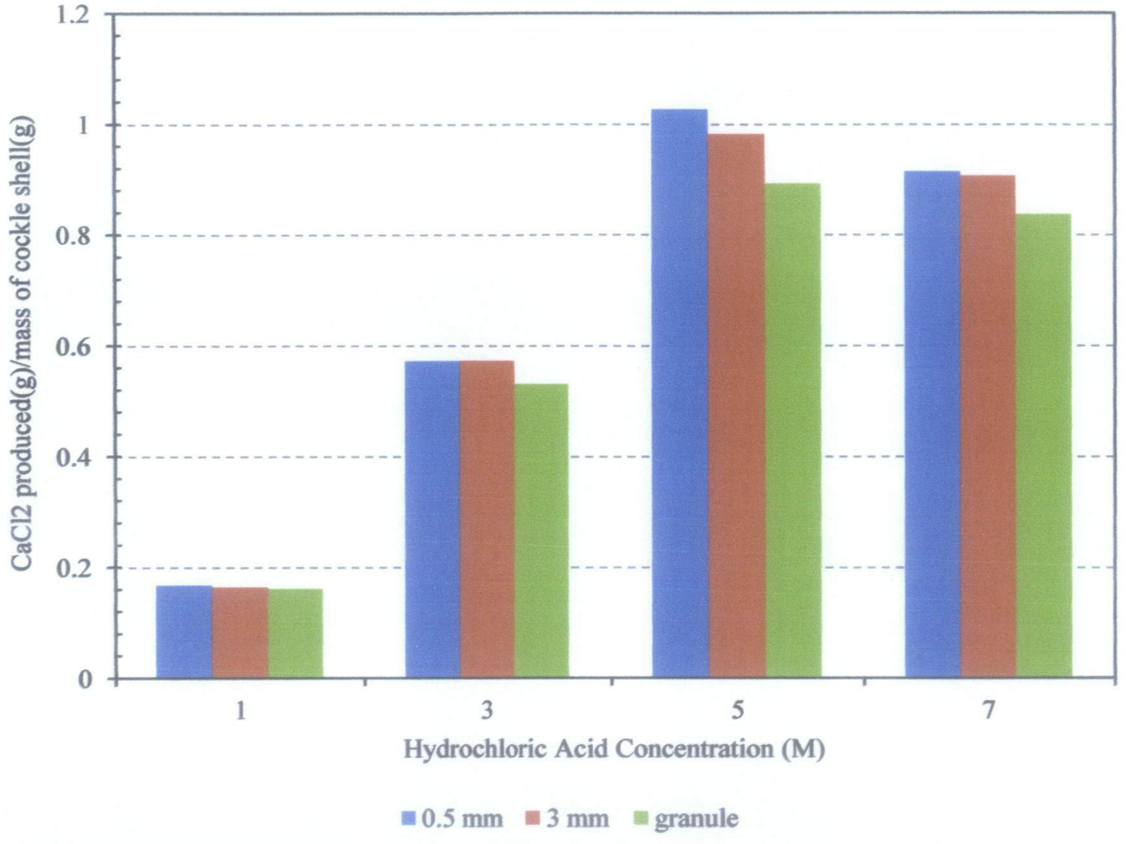


Figure 12: The mass of $CaCl_2$ per gram of cockle shell for different concentration of HCl with different size of cockle shell.

The figure show that the mass ratio of the product to the source (cockle shell) is varies with different concentration of HCl and the size of cockle shell. The highest mass ratio is 1.03 for reacting 5M of HCl and 0.5mm size of particle. The smallest yield is the reaction of 1M of HCl with granule form of cockle shell. The main concern is the highest mass ratio for producing higher product. Referring to this ratio, for reaction 1kg of 0.5mm size of cockle shell with 5M of HCl, it can produce 1.03kg of $CaCl_2$ as the product. The production of $CaCl_2$ was decrease after 5M of HCl due to the impurities limitation of cockle shell. The possible impurities was involve in the reaction is magnesium content in cockle shell. The size of cockle shell was also affect the production of $CaCl_2$ while the mass of cockle shell was including the mass of impurities. The smaller the size of cockle shell, which lead to bigger content of impurities and resulting low production of $CaCl_2$.

4.4 Experiment 4:

Moisture sorption capacity of calcium chloride produced from waste cockle shell, pure calcium chloride and commercial moisture absorber product

In synthesis of calcium chloride using different size of cockle shell and different concentration of hydrochloric acid, it gives 12 products of calcium chloride. In mass production, the highest yield is more favorable to produce larger amount of product. The highest yield product was selected to perform the moisture sorption capacity. 4 grams of each moisture absorbent, which is experiment product (highest yield product), 74% purity calcium chloride and commercialize dehumidifier (Thirsty Hippo) for moisture sorption capacity experiment.

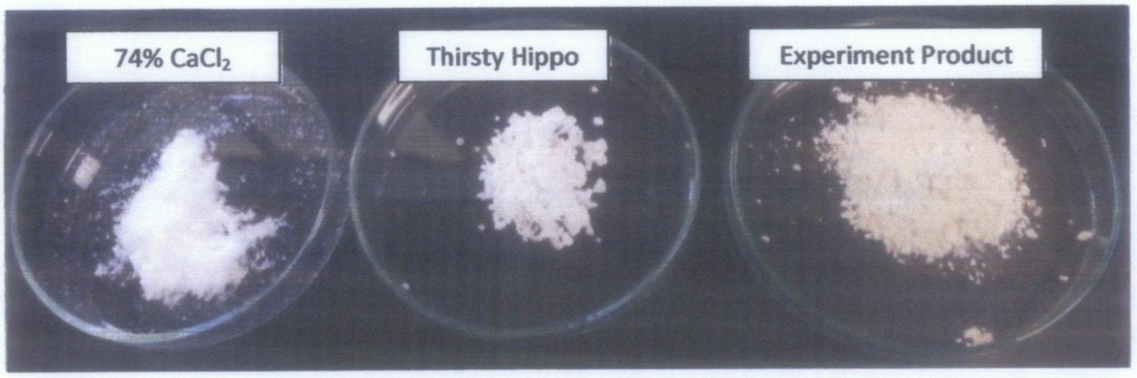


Figure 13: The three different moisture absorbers

The experiment was done under 68% relative humidity and 26°C temperature. The experiment was done in the controlled environment in closed box. Following figure is the overall performance of all the moisture absorbent.

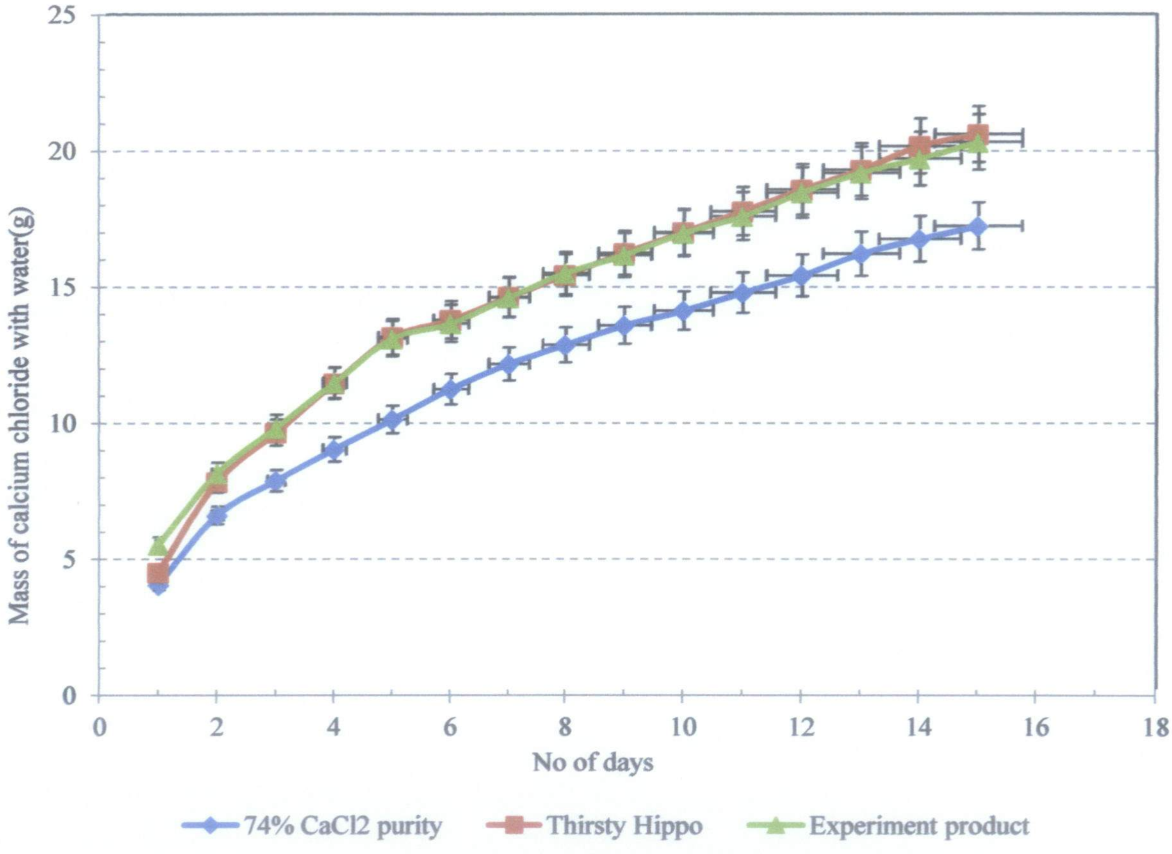


Figure 14: Performance of calcium chloride from different source as moisture absorbent

Table 15 : The experimental kinetic equation of different moisture absorbent.

Moisture absorbent	Kinetics Equation
74% Calcium Chloride	$y= -0.0412x^2 + 1.5213x + 3.3651$
Thirsty Hippo	$y = -0.0566x^2 + 1.9245x + 3.9498$
Experiment Product	$y = -0.0505x^2 + 1.769x + 4.6932$

The performance of the moisture absorbent was evaluated base on the amount of moisture captured by the products. The experiment product is having less than 100% purity of $CaCl_2$ due to trace element in cockle shell. In determine the purity of experiment $CaCl_2$ product, the 74% $CaCl_2$ are using for determine the purity. If the experiment product having higher performance than the 74% purity $CaCl_2$, its mean that the experiment product has more than 74% $CaCl_2$ purity and vice versa. From the result obtained the 74% purity $CaCl_2$ at the lowest performance and below the performance for experiment product. It can be conclude that the experiment product is having more than 74% purity. The performance for the commercialize product and experiment product was comparable. The performance can be said as parallel performance, the result obtained show that the performance of those product are almost the same. The table shows that the experimental kinetics equation for 3 different moisture absorbent which the commercialize product and experiment product having almost the same equation. From this result, as the conclusion, the ability in sorption of moisture using the commercialize product and experiment product is the same. If one package of commercialize can last up to 3 months, the experiment product also having the similar duration.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

As a conclusion, the possibility of producing moisture absorber from *Anadara granosa* waste can be determined by this experiment. The methodology was focused on the concentration and size of cockle shell parameter. The quality of the produced moisture absorber (calcium chloride) was comparable to the commercial moisture absorber in moisture sorption capacity with having more than 74% purity. The performance of experiment product and commercialize is almost the same and can be conclude that the absorption duration commercialize dehumidifier is same with the experiment product. The highest yield is 25.678g from combination of 0.5mm size of cockle shell and 5M of hydrochloric acid. The 1kg of cockle shell can produce 1.03kg of calcium chloride is the best mass ratio in this experiment.

The future plan would be to characterize the element quality of the sample and the product. For the best analysis of the products which is calcium chloride by using inductively coupled plasma mass spectrometry (ICP-MS). This approach is to determine the components percentage in the sample and the product for sample and product specification. The other recommendation is to perform the performance experiment until it reach the maximum capacity of moisture absorbed for all type of moisture absorbent. The successful of this project may lead to large scale synthesis of calcium chloride from a low cost but abundant natural resource which is cockle shell wastes.

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APPENDICES

Appendix 1: Raw Data Experiment 3

Experiment for 1M HCl

Size of cockle shell	$CaCl_2$ produced (actual yield) (g)	Time to complete reaction (mins)	$CaCl_2$ produced (actual yield) (g)	Time to complete reaction (mins)	$CaCl_2$ produced (actual yield) (g)	Time to complete reaction (mins)	$CaCl_2$ produced (actual yield) (g)	Time to complete reaction (mins)
	First Trial		Second Trial		Third Trial		Average	
0.5 mm	4.101	40	4.506	45	4.011	35	4.206	40
3 mm	4.308	70	4.012	80	4.04	75	4.12	75
granule	3.962	130	4.203	125	4.012	120	4.059	125

Experiment for 3M HCl

Size of cockle shell	$CaCl_2$ produced (actual yield) (g)	Time to complete reaction (mins)	$CaCl_2$ produced (actual yield) (g)	Time to complete reaction (mins)	$CaCl_2$ produced (actual yield) (g)	Time to complete reaction (mins)	$CaCl_2$ produced (actual yield) (g)	Time to complete reaction (mins)
	First Trial		Second Trial		Third Trial		Average	
0.5 mm	13.996	30	14.506	35	14.476	31	14.326	32
3 mm	14.031	65	14.496	60	14.52	55	14.349	60
granule	12.856	90	13.365	105	13.658	105	13.293	100

Appendix 1: Raw Data Experiment 3 (continued)

Experiment for 5M HCl

Size of cockle shell	$CaCl_2$ produced (actual yield) (g)	Time to complete reaction (mins)	$CaCl_2$ produced (actual yield) (g)	Time to complete reaction (mins)	$CaCl_2$ produced (actual yield) (g)	Time to complete reaction (mins)	$CaCl_2$ produced (actual yield) (g)	Time to complete reaction (mins)
	First Trial		Second Trial		Third Trial		Average	
0.5 mm	26.023	25	24.353	20	26.353	24	25.678	23
3 mm	25.145	30	23.698	36	24.858	33	24.567	33
granule	23.096	65	21.465	70	22.456	69	22.339	68

Experiment for 7M HCl

Size of cockle shell	$CaCl_2$ produced (actual yield) (g)	Time to complete reaction (mins)	$CaCl_2$ produced (actual yield) (g)	Time to complete reaction (mins)	$CaCl_2$ produced (actual yield) (g)	Time to complete reaction (mins)	$CaCl_2$ produced (actual yield) (g)	Time to complete reaction (mins)
	First Trial		Second Trial		Third Trial		Average	
0.5 mm	22.679	9	23.413	8	22.545	7	22.879	8
3 mm	22.238	12	23.369	10	22.418	8	22.675	10
granule	20.897	20	21.023	22	20.888	18	20.936	20

Appendix 2: Raw Data Experiment 4

Time	Mass of Cacl2 solution(g)					
	Pure		Thirsty Hippo		experiment	
Initial weight= mass of pantry dish + 4 gram product	54.547	Moisture Captured(g)	52.735	Moisture Captured(g)	58.427	Moisture Captured(g)
1	58.598	4.051	57.233	4.498	63.952	5.525
2	61.144	6.597	60.568	7.833	66.564	8.137
3	62.419	7.872	62.376	9.641	68.234	9.807
4	63.567	9.02	64.184	11.449	69.899	11.472
5	64.665	10.118	65.884	13.149	71.519	13.092
6	65.784	11.237	66.513	13.778	72.077	13.65
7	66.709	12.162	67.356	14.621	73.025	14.598
8	67.407	12.86	68.158	15.423	73.917	15.49
9	68.126	13.579	68.967	16.232	74.586	16.159
10	68.662	14.115	69.733	16.998	75.384	16.957
11	69.322	14.775	70.499	17.764	76.012	17.585
12	69.954	15.407	71.298	18.563	76.876	18.449
13	70.751	16.204	72.029	19.294	77.6	19.173
14	71.298	16.751	72.897	20.162	78.124	19.697
15	71.772	17.225	73.331	20.596	78.734	20.307