WOLKITE UNIVERSITY

COLLEGE OF ENGINEERING AND TECHNOLOGY

DEPARTMENT OF CHEMICAL ENGINEERING

PREPARATION OF CALCIUM ACETATE FROM EGG SHELL AND APPLICATION FOR PHOSPHATE REMOVAL

The project submitted to the College of Engineering and Technology, department of Chemical Engineering in partial fulfilment of the degree of bachelor of science in Chemical Engineering

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Declaration

We, the undersigned, declare that this thesis entitled "preparation of calcium acetate from egg shell" is a result of our effort and hard work. It is our original work, and has not been presented for the award of a degree in any university, and all the sources of materials used for this thesis have been duly acknowledged.

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This thesis has been submitted for examination with my approval as a university advisor.

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Acknowledgment

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List of abbreviation and acronym

FTIR:	Fourier transform infrared Spectroscopy
UV-VIS:	ultraviolet-visiblespectrophotometry
NPV:	Net present value
NFW:	Net future worth
HAp	hydroxyapatite
SCIL	Safer Chemical Ingredients List
EPA	Enviromental protection agency
FAO	Food and agricultural organization
WHO	World health organization

Abstract

Calcium acetate is the calcium salt of acetic acid. It is used, commonly as a hydrate, to treat hyperphosphaspataemia (excess phosphate in the blood) in patients with kidney disease: the calcium ion combines with dietary phosphate to form (insoluble) calcium phosphate, which is excreted in the feces. In this study, calcium acetate was prepared by using eggshell and vinegar for the purpose of minimizing high raw materials cost, energy consumption, and energy wastage. The effects of concentration and extraction time was determined. Egg shell was reacted with acetic acid at different conditions (concentration at 2M,4M and 6M and reaction time 1,2 and 3 hrs.). The maximum effect were chosen based on the maximum yield of calcium acetate. Afterwards, the prepared calcium acetate was used to remove phosphate ion from a solution. Generally maxium effect for calcium acetate preparation was found to be at 6M, for 3hrs.

Key words: Calcium acetate, eggshell, and phosphate ions

CHAPTER ONE

1. INTRODUCTION

1.1 Background:

Calcium acetate is the food that grew up the in recent years reinforce of replenishing the calcium, and its purposes is extremely extensive, at the calcium supplement of pharmaceutical industries as humans and animals; Be used for toothpaste at light industry as scale remover; In foodstuffs industry, calcium acetate is a kind of safe foodstuff additive, stabilizer and thickening material etc.; Calcium acetate also is considered to have the fodder additives of potential market value most and is used for aquaculture; It participates in the formation of bone and building again of fracture back osseous tissue as medicine, participates in Muscle contraction, neurotransmission, glandular secretion, vision physiological and clotting mechanism etc. The raw material that is used for the calcium acetate preparation at present is calcium oxide and lime carbonate mostly, and these two kinds of raw materials all need the suitability for industrialized production preparation, and the problem that prior art exists is that raw materials cost is higher, and energy consumption is big, the waste resource. [1]

Calcium acetate is used to control high blood levels of phosphorus in people with kidney disease who are on dialysis (medical treatment to clean the blood when the kidneys are not working properly). Calcium acetate is in a class of medications called phosphate binders. It binds phosphorus that you get from foods in your diet and prevents it from being absorbed into your blood stream.

Calcium acetate is an effective phosphorus binder in patients with renal failure. Calcium salts are increasingly used as phosphorus binders in patients with chronic renal failure. Calcium carbonate is the principal salt presently utilized, however, other calcium salts may be more effective and safer phosphorus binders. Theoretical calculations, in vitro experiments, and in vivo studies in normal subjects have shown calcium acetate to be a more effective phosphorus binder than other calcium salts. This salt has not previously been studied in patients with chronic renal failure.

We used a one-meal gastrointestinal balance technique to measure phosphorus absorption, calcium absorption and phosphorus binding in six patients with chronic renal failure. Calcium acetate was compared with calcium carbonate and placebo. [2] Eggshells contain high amounts of $CaCO_3$ (94–97%), some proteins (3–4%), and minor traces of MgO, P_2O_5, K_2O [1,2]. Calcium carbonate has the highest concentration of elemental calcium (40%). Its bio availability is low due to the fact that it is soluble only in strongly acidic environments, and as a result, a low absorption rate of Ca ions occurs in the gastrointestinal tract where the pH is neutral or alkaline. The very high content of calcium carbonate allows the use of these eggshell powders as a raw material for obtaining organic calcium in the form of calcium acetate, which is water soluble, generally regarded as safe, tasteless and has high absorptive properties by the human body. Adequate calcium intake contributes to the prevention of calcium deficiency in the elderly and in children. [3]

1.2 Statement of the problem

Eggshell is a household and cafeteria waste in Ethiopia. Every year, many tones of it is discarded as a solid waste. [4] This huge amount of solid waste demands to be dealt with and costs hundreds of thousands of birr tax payers' money. Not only that, the government pays the little foreign currency it has on importing medication for kidney and blood disorder patients. These two problems can be solved simultaneously by preparing calcium acetate from waste eggshells by mixing it with acetic acid in industrial scale and purifying it to the level of human consumption. Besides it used as an absorbent to remove harmful ions like phosphate and nitrate from wastewater farm runoff from farms.

1.3 Objectives of the study

1.3.1. General objective of the study

The general objective of the study is preparing Calcium Acetate from eggshell and its application on removal of phosphate ion from solution.

1.3.2. Specific objectives of the study

- ✓ To optimize the extraction conditions(concentration and extraction time).
- ✓ To apply calcium acetate as a possible absorbent for Phosphate ion removal from waste water.

1.4 Significance of the Study

The significance of this project can be seen in three perspective i.e. environmental, economic, and social perspective and it is discussed in detail below here:When it is considered with respect to environmental pollution eggshell is one of the solid waste that has an impact on environment.[5] This project is significant to eliminate or reduce this problem by reuse the solid waste for calcium acetate production and help the government by regulating the environmental policy. When it is considered with respect to the economical aspect in our country calcium acetate is used in many hospitals. The current demand of calcium acetate production in Ethiopia is not covered by domestic production. Most of the supply required by the country is satisfied through import. Therefore, this project aims to help the country to have sustainable economic development by satisfying the need of calcium acetate and via import substitution.

When it is considered with respect to the social aspect which is important by create job opportunity to the community and give the final product of calcium acetate by compromise price to the customer in the society. There is also significant to the society by providing infrastructure like road network etc. to the society.

1.5 Scope of the Research

The scope of this project is to prepare calcium acetate from waste eggshell and acetic acid. It also aims to determine the effect of concentration, and extraction time on the yield of the product. Furthermore, it will apply calcium acetate for the removal of phosphate ion from waste water.

CHAPTER TWO

2. LITERATURE REVIEW

2.1 What is a Calcium Acetate?

Calcium acetate is one of the essential minerals that the human body require to function properly. Calcium plays a great role in bone formation and its growth and maintenance. . Moreover, can also join with other minerals like phosphate and help in their removal from the human body. Furthermore, calcium acetates in controlling the phosphate levels and eliminates its negative implications on human body. Calcium Acetate is is a chemical that is primarily a calcium salt of acetic acid. It is also known as acetate of lime. The formula of calcium acetate is $C_4H_6CaO_4$. Even though this compound is commonly known as calcium acetate. Moreover, calcium acetate is colourless, and it is a white crystalline solid, which smells slightly like acetic acid. It is soluble in water and alcohol but insoluble in acetone and benzene. This compound is strongly hygyroscopic when it is in its an hydrous form and arrives as mono hydrate in its regular form. Furthermore, this chemical can be gathered by soaking calcium carbonate in a vinegar solution. Calcium acetate has not been found yet as a free compound in nature. Moreover, it is mainly used in producing various medicines, food additive , sequestrate , buffer, etc.

2.2 Formula and structure

Calcium acetate and acetate of calcium ethanoate or lime is a substance which has a a variety of use in medicine. Additionally, it aids individuals suffering from kidney diseases by regulating phosphate levels in their body. The calcium acetate formula is $C_4H_6CaO_4$. Moreover, its extended formula is $Ca(CH_3COO)_2$.Furthermore, the calcium acetate structure suggests that one calcium cation (Ca^{2+}) and two acetate anions (CH_3COO^-) forms this salt. Moreover, it is very hygroscopic, and it is commonly found as hydrated salts.

2.3 Properties Of Calcium Acetate

Physical properties of Calcium acetate

- Calcium acetate is a white, hygroscopic compound . it has an odor of acetic acid.
- Its density is $1.509 gm_l^{-1}$.
- Additionally, its melting point is 160 ^oC.
- Furthermore, it is completely soluble in water and alcohol, and partially in methanol.

However, it is insoluble in acetone and ethanol. However, it is insoluble in acetone and ethanol.

Chemical Properties of Calcium Acetate

Calcium Acetate is a chelator which means this molecule is capable of forming a different coordinated bond called ‘chelation’, since it has one metallic atom, i.e . calcium, which can bond with other chemical ions, thus , calcium acetate can do the same. Moreover, the calcium atoms present in this molecule are extremely helpful in regulating the phosphate level in the blood . the reason being this calcium acetate reacts and produces phosphate , which is insoluble . hence it is excreted without any hastle.

Table1:Chemical properties of calcium acetate

Chemical formula	**$C_6H_6CaO_4$**
Odor	**Like acetic acid**
Density	**1.509cm^3**
Solubility in water	**29.7g/100ml(100 ^{0}c)** **34.7g/100 ml(20 ^{0}c)** **37.4g/ 100 ml(10 ^{0} c)**
Molecular weight	**158.166g/mol**
Acidity	**Ca, 0.7**
Melting point	**160^{0}c**

2.4 Preparation Of Calcium Acetate

Calcium acetate uses calcium carbonate found in eggshells, or rocks like limestone or marble for its preparation. After that, this calcium carbonate is soaked in acetic acid like vinegar to reach the result. The equation of this process is :

$CaCO_3(s) + 2CH_3COOH(aq) \rightarrow Ca(CH_3COO)_2(aq) + H_2O(l) + CO_2(g)$ Ca(OH) 2(s)

$+ 2CH_3COOH(aq) \rightarrow Ca(CH_3COO)2(aq) + 2H_2O(l)$

Furthermore, when lime is used for this reaction, it passes an acetic acid vapor over the heated mineral. Calcium preparations contain carbonate, citrate, or gluconate salts which are not always effective. Because of that, natural sources of minerals and vitamins are becoming more popular. Eggshells can be alternatively used as a natural source of calcium and are characterized by higher solubility when compared to currently used oyster shells .The eggshell consists of 95% of calcium carbonate, 3.5% of glycoproteins, and proteoglycans. The inner shell membrane contains glucosamine, chondroitin sulphate, hyaluronic acid, type I collagen, and a high amount of proteins and micro-elements such as magnesium, strontium, zinc, barium, fluorine, which could have positive effects on bone metabolism .It has been noted that the powder from eggshells has desirable properties, such as easy ionization at low stomach pH and high calcium content (36–39%). It was also proved that the natural powder of inner shellmembranes significantly decreases joint stiffness, reduces pain and inflammatory condition in patients with osteoarthritis. 37% of eggshell calcium is in the form of carbonate with low bio availability for the organism. According to these reports, a new technology of eggshell processing was developed. Eggshells were roasted in the presence of citric acid [4]

2.5 Raw Materials used for the production of calcium acetate

2.5.1 Eggshell

Eggshell is a solid waste, with production of several tons per day. Eggshell is mostly sent to the landfill with a high management cost. It is economical to transform the eggshell waste to create new values from these waste materials. The eggshell waste can be used (a) at bio diesel production as a solid base catalyst used for bio diesel pollutants minimization, reducing the production costs of bio diesel and making the process of bio diesel production fully ecological and environment-friendly; (b) as an absorbent of heavy metals from wastewater as it is a serious environmental problem in the ecosystem;(c) as bio material in order to replace bone tissues due to the rise in the number of patients; (d) as a fertilizer and calcium supplement in nutrition for human animals, plants, etc. Number of research articles have been included in this review to describe a methodical growth in this subject matter.[6]

2.6 Factors Affecting the Quality of the Product

Quality of the calcium acetate can be affected by different factors such as time, temperature, acetic acid concentrations, particle size and other minor factors. However, none of these factors are equally contributes to the quality of the product. Out of these factors affecting the quality of the product, temperature, time and acetic acid concentration are the most relevant factors due to their significance influence.

2.7 Uses of calcium acetate

- Calcium acetate is primarily used to regulate the blood pressure of dialysis patients. Even though, dialysis removes phosphate from an individual's body, it may not prove enough. Hence, the use of calcium acetate tablets is other medications that can remove enough phosphate
- Besides removing this excess phosphate prevents unsafe materials from gathering in the human body, and keeps the bones strong. It also reduces the possibility of any heart diseases and strokes.
- Additionally , due to its inexpensive nature, calcium acetate was used as a starting material for acetone synthesis. However. After the introduction of the cumene process , this practice has stopped . The chemical formula of this process is,

  $Ca(CH_3COO)_2 \rightarrow CaCO_3(s) + (CH_3)_2CO$

  Tofu is traditionally prepared by soy milk and calcium sulphate . However, calcium acetate has proved to be a better alternative for this purpose. It is soluble and requires a smaller amount.

The process of using calcium acetate

If any one is using it with a doctor's recommendation, they must ensure proper dosing. It will completely depend on a particular patient's medical condition and he/ her current treatment. Moreover, the timing of having this medication is also crucial. Typically, it is taken during a meal via the mouth. If any one is using calcium acetate medicine in its liquid form , then it is vital to use a medication- measuring device instead of a house hold spoon. Since overdosing of it is unsafe; thus, a precision dose is essential. Furthermore, , taking calcium acetate every day is essential to reap its benefits. However, follow the volume and schedule prescribe by the doctor. Additionally, do mot increase or decrease its usage without consult a doctor, as it can have side effects.

Medical application of eggshell

Agricultural wastes contain active compounds that are valuable in medical applications Regarding this feature, bio-compatible material or bio material production from them has added a different dimension to the utilization of agricultural waste. An insight into utilization of avian eggshell as an agricultural waste, is to produce HAp. A calcium phosphate ceramics material was found to be crucial as a bio-material because of its osteophilic nature and its incorporation into bone tissues [7] Discarded eggshells remain largely unutilized and untransformed. The eggshells consist of calcium carbonate as a useful material to produce HAp, which is the majorinorganic part in bones used in bone and dental therapy. Moreover, the use of eggshell to produce HAp will help reduce the pollution effect of the waste and the subsequent conversion of the waste into a highly valuable product as a good chance of reducing the cost of treatment in bone repair or replacement with little impact to the environment. The process of transforming eggshell into HAp and nano-HAp is an environmentally friendly process. proposed a research of the chicken eggshells recycling as a way of improving the ecosphere; by reduction of waste management requirements and utilization of eggshells as useful raw materials for nanomaterials. The main component and the major inorganic substance in eggshells are calcium carbonate (calcite) and it makes up about 94% of chemical composition of eggshell. This makes it an essential material for Hap production-eggshell is a rich source of minerals, serving as a pharmaceutical excipient, a base material for developing medicinal and dental preparations, a food additive and calcium supplement, a diluent of solid dosage forms, an agricultural fertilizer component, and as a component for bone implants.

Summary of Petition [Calcium Acetate]:

Calcium acetate can occur naturally but is more often formulated by chelating finely ground limestone (calcium carbonate) with acetic acid. During this process calcium acetate is formed and comprises about 5% of the calcium in the final product. The remainder of the final product is primarily calcium carbonate. Other materials such as xantham gum and/or humic acids may be added to make a proprietary product. Calcium acetate has a variety of potential uses. This petition asks for approval for organic use as a soil amendment, plant micro nutrient, soil pH adjuster and as a sun-scald protectant.

Calcium acetate is also currently registered for yellow jacket control in conventional crops. In each of these uses, the calcium acetate product is mixed with water and applied by spray to the crop, soil, or structure/covering. In the crops/soils use, the calcium acetate has an advantage in that it is much more water soluble than calcium carbonate and is more readily available to the plant. Other traditional sources of calcium, such as calcium carbonate, do not become water soluble until they have been acted on by soil microbes or acidic conditions. Products that include calcium acetate as well as other slower acting calcium sources can have both an immediate impact on the plant as well as an extended release effect as thoseless soluble materials are made plant available. For sun scald protection, the material acts to block direct transmission of sunlight due to its opacity. Sun scald occurs when exposure to sunlight overheats crops and causes scarring. This scarring can affect keeping quality, cosmetic appearance, taste, and texture. An aqueous mixture containing calcium acetate may be sprayed on black plastic to lower soil temperatures or as a coating on greenhouses to lower inside temperatures. The opacity of the material is primarily due to the calcium carbonate remaining in the product after the calcium acetate is formed (2018 TR). [8]

Category 1: Classification 1.

For crop use: Is the substance Non-synthetic x Synthetic?

Is the substance formulated or manufactured by a process that chemically changes a substance extracted from naturally occurring plant, animal, or mineral sources? If so, describe, using NOP 5033-1 as a guide. Calcium acetate is made from finely ground limestone which is chelated with acetic acid. It is a naturally occurring substance, which is produced and broken down in the metabolic cycles of humans and animals (2018 TR), however, it is most commonly synthesized by the neutralization of acetic acid and calcium carbonate. The petitioner and the 2018 TR both state that the material is synthetic. 2. Reference to appropriate OFPA category: Is the substance used in production, and does it contain an active synthetic ingredient in the following categories: copper and sulfur compounds; toxins derived from bacteria; pheromones, soaps, horticultural oils, fish emulsions, treated seed, vitamins and minerals; livestock parasiticides and medicines and production aids including netting, tree wraps and seals, insect traps, sticky barriers, row covers, and equipment cleansers; or (ii) is used in

production and contains synthetic inert ingredients that are not classified by the Administrator of the Environmental Protection Agency as inerts of toxicological Concern. The petitioner is asking for calcium acetate to be classified as a synthetic compound under vitamins and minerals. In its use as a plant micro nutrient or, possibly, as a pH adjuster, the use would fall under minerals. For its use as a sun-scald protectant or shading material it could be interpreted as a production aid.

Category 2: Adverse Impacts

1. What is the potential for the substance to have detrimental chemical interactions with other materials used in organic farming systems? Calcium is widely used and available in agricultural ecosystems and calcium acetate is simply a more soluble form of calcium that is rapidly bio available. In general, calcium products are positive additions since calcium forms the building blocks of cell structures and functions. However, the 2018 TR notes two potential negative impacts. First, calcium acetate could bind phosphates, thus making them unavailable to plants as a nutrient source. This would primarily happen with the improper use of phosphoric acid. Phosphoric acid is only approved as an equipment cleaner and should have no direct contact with organically managed land or livestock. Secondly, if Over applied it could cause an over adjustment of pH and could result in increased soil alkalinity.

2. What is the toxicity and mode of action of the substance and of its breakdown products or any contaminants, and their persistensce and areas of concentration in the environment? The 2018 TR states that there are no published studies on the environmental persistence of calcium acetate. Various EPA documents are cited noting that calcium acetate may be present in the metabolic cycles of animals; therefore, no risk is posed to the environment. The EPA has placed calcium acetate on the Safer Chemical Ingredients List (SCIL) for processing aids and additives as a safer replacement for traditional ingredients. Moreover, the EPA has designated calcium acetate as “verified to be of low concern based on experimental and modeled data,” and has “not identified any toxic endpoints for birds, plants, aquatic, or soil organisms” (2018 TR).

.In general, the environmental impacts of this material should be minimal, but the 2018 TR notes that the greatest potential for environmental degradation is the mining necessary to source the calcium carbonate.

This mining could degrade or disrupt ground water, surface water, and ecosystems in the vicinity of the mine and could cause contamination from spills. There could also be additional carbon dioxide released to the atmosphere due to fossil fuel burned by mining equipment.

3. Discuss the effect of the substance on human health.

Calcium acetate is widely used for human health as treatment for calcium deficiency and to treat patients with hyperphosphatemia in end stage renal disease. It can be used as a stabilizer and preservative in many food substances. The 2018 TR quotes various sources in that it has been authorized for human consumption without limitation by the Joint FAO/WHO Expert Committee on Food Additives, FDA has granted it GRAS status as a sequestrant and direct food substance, and EPA has placed it on the Safer Chemical Ingredients List for processing aids and additives.

4. Discuss any effects the substance may have on biological and chemical interactions in the agroecosystem, including the physiological effects of the substance on soil organisms (including the salt index and solubility of the soil), crops and livestock. When used as petitioned, calcium acetate is applied as an aqueous mixture with calcium carbonate. While the calcium carbonate could provide calcium, it is not readily absorbed by plants. Calcium acetate has been reported to increase plant absorption of calcium ions (Ca^{2+}) compared to salts with other organic and inorganic anions (e.g., lactate, citrate, oxalate, chloride, nitrate) .Calcium is necessary for cell wall formation and stabilizes lipids within cell membranes. It helps to regulate cell processes such as transport across cellular membranes and enzymatic functions. It may also aid in the uptake of other micronutrients and may increase the storage life of fruits and vegetables. Common symptoms of insufficient calcium in fruits and vegetables include blossom end rot in tomatoes and bitter pit in apples. Calcium is common in the environment and the application of calcium acetate simply makes calcium more readily available for absorption. EPA has “not identified any toxic endpoints for birds, plants, aquatic, or soil organisms” so the application of calcium acetate should not have negative ecosystem effects except in the case of where it might be over applied and create excess soil alkalinity.

5. Are there any adverse impacts on biodiversity?

There are no published studies on the environmental impacts of calcium acetate;

however, the EPA has “not identified any toxic endpoints for birds, plants, aquatic, or soil organisms” (2018 TR) The 2018 TR goes on to note that calcium acetate acts as a water-soluble and bio available source of calcium, especially important in soils with high pH. The petitioned substance also increases the pH of the soil. Additionally, when used as petitioned, the substance can provide protection from sunscald as well as act as a mechanism for regulating plant temperature due to the opaque nature of the applied liquid. Once introduced into agricultural soils, the salt may result in several different outcomes, including absorption by plants, reacting with acidic chemicals in the soil, or dissolving and entering water systems, depending on the environmental conditions of the soil

CHAPTER THREE

3. MATERIALS AND METHODS

3.1.1 Equipment

The following equipment were used during the study.

- ✧ Mass balance ;to measure the mass of raw materials and products.
- ✧ Beaker ;to hold our samples
- ✧ Hot plate;to evaporate the moisture's
- ✧ Measuring cylinder ;to measure the volume of chemicals .
- ✧ Ball mill;for size reduction.
- ✧ Oven ;for drying.
- ✧ Uv- vis spectroscopy;to characterize the phosphate removal.

3.1.2 Chemicals used

- ❖ Egg shell
- ❖ Distilled water
- ❖ Ca(CH3COO)2
- ❖ H_3PO4

3.2 METHODS

3.2.1 Experimental frame work

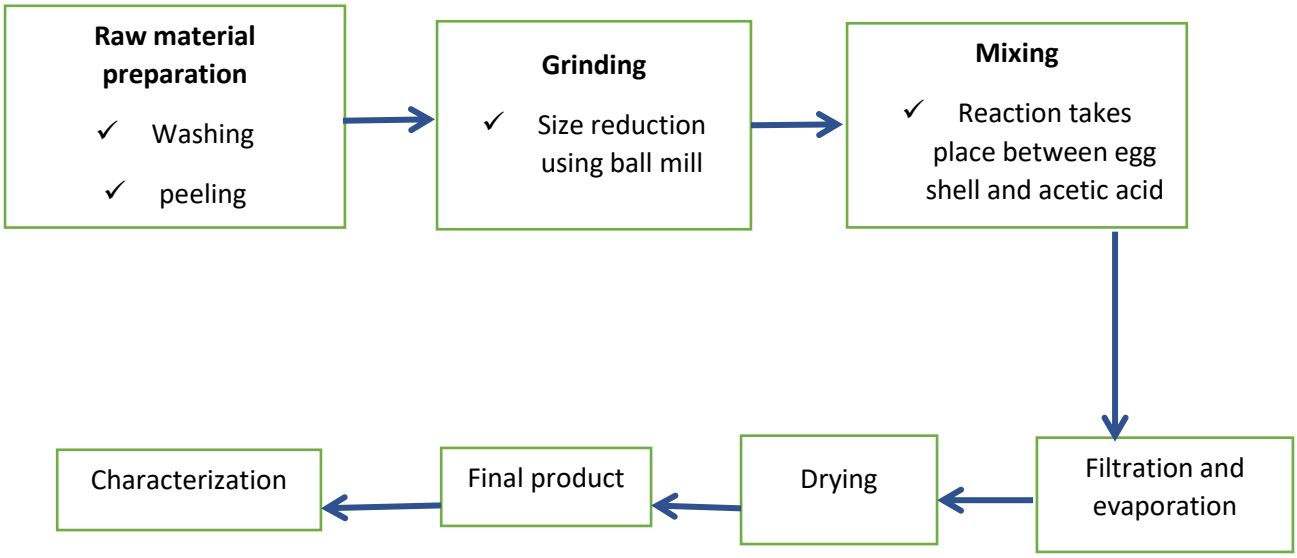


Figure 1:block flow diagram of the experimental frame work

3.2.2 Process Description of Calcium acetate production from eggshell and acetic acid .

Preparation and collection of raw material

First the egg shells were collected from different restaurants and households. Then, the collected egg shell was washed, and the ones with too much dirt or discoloration were discarded.

Washing

The egg shell was washed well, and it is boiled for 10 minutes to remove the thin film on the inside of egg shells.

Size reduction

The purified eggshells were grounded to powder to prepare them for the reaction with acetic acid. Then, the cleaned and dried eggshell were milled in ball mill and sieved with size of 250 micro meter.

Mixing

50 gm of powder egg shell was weighed and mixed with 150 ml of diluted acetic acid in a beaker with stirrer for an hour. The egg shell was reacted with different concentrations of acetic acid (2M,4M and 6M) and at different reaction times of (1 ,2 and 3 hrs.). 9 distinct experiments were conducted.

Filtration

After the mixing process had been completed, the solution was filtered and the residual calcium acetate obtained in the mixing process at that specified combination of the factors was recorded for each experiment.

Evaporation

The clear filtrate was heated on a hot plate to evaporate the water and obtain a white cake.

Drying

The moist calcium acetate was dried in an oven for 3 hours at 80-degree Celsius.

Characterization

The calcium acetate, calcium phosphate from the phosphate removal, and eggshell powder were characterized by physiochemical methods in case of unavailability of equipment used for characterization while the removal of phosphate ion from the solution checked by uv-vis spectroscopy.

The pH of Calcium Carbonate and calcium acetate was determined. They were dissolved in distilled water. The pH of the product were determined by using PH meter by immersing it in the solution.

Procedure we undertaken to calculate mass percentage of calcium carbonate

1 Preparation of the Eggshell

- The shell was washed with distilled water and peeled off all of the membranes from the inside of the shell.
- The shell was dried for about 20 minutes.
- It was grounded to a very fine powder using ball mill.

2 Dissolution of the Eggshell in Excess HCl(aq)

- ✓ The egg shell was weighed accurately (1.00g) and added to a beaker of 1M HCl (25cm3).
- ✓ The solution was stirred until all carbonate was dissolved and added to a

volumetric flask (250cm3).

3 Titration of the Unreacted HCl(aq) With ~0.1 M NaOH(aq)

- ❖ Three flask were prepared and **HC**l was added to each of them.
- ❖ 3-4 drops of phenolphthalein indicator was added to each flask
- ❖ The buret was filied with ~0.1 M NaOH solution.
- ❖ Initial volume were read and recorded to ± 0.01 mL.
- ❖ Titrate one sample to the first persistent barely-pink color.
- ❖ When you are close to the endpoint the color will fade slowly. Add more ~0.1 M NaOH(aq) dropwise until the color remains for at least 30 seconds.
- ❖ The final volume was read and recorded to ± 0.01 mL.
- ❖ The titration was repeated for the other two samples.

Calculations

- **We have recorded three volume of titre**

Table 2:titration of calcium carbonate

	Titre 1	**Titre 2**	**Titre 3**
Titre volume(ml)	**6.2**	**6.0**	**6.2**

Avarage titre volume= $\frac{6.2+6.0+6.2}{3}$ = 6.1

CaCO3 + 2HCl ⟶ CaCl2 + H2O + CO2

HCl + NaOH ⟶ NaCl + H2O

Average Titre of **NaOH = 6.1mL**

Concentration of **NaOH = 0.1 mol/l**

n(NaOH) = C x V

n = 0.1 x 0.0061

n = 6.1x10-4 moles

1:1 NaOH: HCl

n = 6.1x10-4 moles: n = 6.1x10-4 moles x10 (scaling up for volumetric flask)

n = 6.1x10-3 moles

Original moles of acid = **n x c**

n = 1 x 0.025 **n** = 0.025moles

Moles of unreacted acid = 0.025 moles - **$6.1x10^{-3}$** moles = **0.0189 moles**

1:2 CaCO3 : HCl

0.0189 / 2 = **9.45 x 10-3 moles of CaCO**3

M = n x GFM

M = 9.45x10-3 moles x 100.1 g/mol

M = 0.945g

% Purity = Calculated Mass / Sample Mass x 100

% Purity = 0.945 / 1.00 x 100 = 94.6%

3.2.3. Solubility of calcium acetate

calcium acetate is a white crystalline solid, which smells slightly like acetic acid.

We have observed the solubility of calcium acetate in water ,alcohol,and acetone.

3.2.4.Characterisation of Calcium Phosphate Ca3(PO4)2

Calcium phosphate compound appears to be either crystalline or white amorphous powder that is tasteless and odorless. It is insoluble in acetic acid and ethanol but soluble in hydrochloric acid and dilute nitric acid. Also, it slightly dissolves in water and is found in milk, bones, teeth, and ground.

3.3. Experimental procedure for preparation of calcium acetate at concentration and time

First, egg shells were collected from gubre restaurants and campus lounges. Next, it was washed, boiled, and dried in order to remove proteins and dirt. Then, the cleaned and dried eggshell was milled in ball mill and sieved with size of 250 micro meter. After that, the egg shell powder was reacted with different concentrations of acetic acid [2M,4M and 6M] at different reaction times of {1 ,2 and 3}.9 experiment were conducted with these two factors .

After reaction, the product was filtered using filter paper and then the water was evaporated by using hot plate in order to remove all the moisture. The product was put in an oven for drying, and after that mass of each run was measured.

3.4 Methods for Phosphate Removal

3.4.1 Experimental frame work

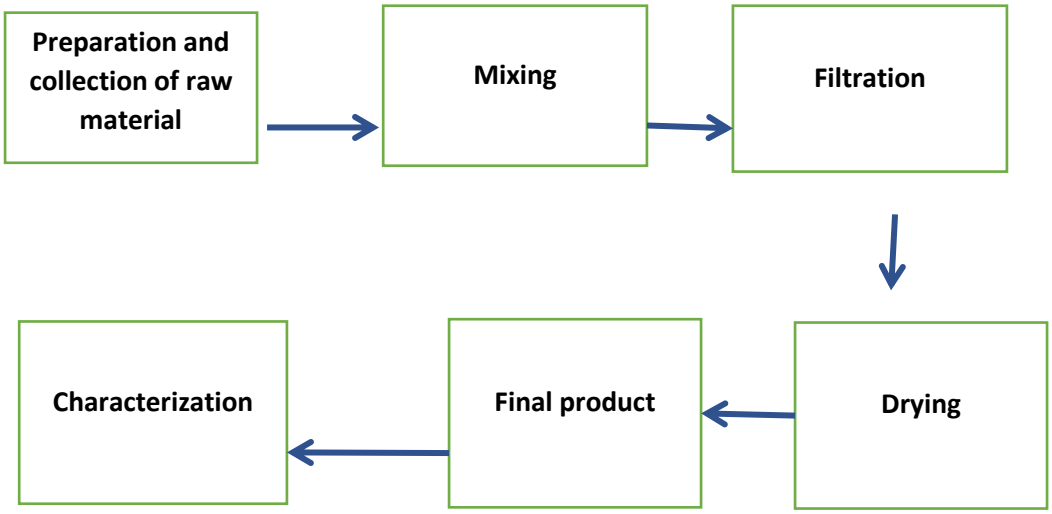


Figure 2:experimental frame work of removal of phosphate ion

Preparation and collection of raw material

Mixing and filtration

59.3g of calcium acetate was weighed and mixed with 500 ml of diluted phosphoric acid in a beaker with stirrer for different hours. After that, the residual calcium phosphate obtained in the mixing process was filtered.

Drying

The filtered calcium phosphate was dried in an oven for 3 hours at 100 ^{o}c to get a powder calcium phosphate.

Characterization

Calcium phosphate was characterized by physiochemical method whiles the removal of phosphate ion from the solutio was checked by uv-vis spectroscopy.

Procedures undertaken to determine the absorbance of calcium acetate for phasphate removal

1. 5,10,15,and 20 mg/l of calcium acetate standard were prepared from product and 100ml of waste water from bath.
2. 35ml sample was taken in to 100ml beaker.
3. 10ml vanadate molybdate reagent was added.
4. 5ml of distilled water was added.
5. After 10-15 min the absorbance of calcium acetate was read at 470nm by using uv -spectroscopy.

CHAPTER FOUR

4. RESULT AND DISCUSSION

Table 3 physio chemical properties of CaCo3,Ca(CH3COO)2 and Ca(PO4)2

Physio-chemical properties	CaCO3	Ca(CH3COO)2.	Ca(PO4)2
pH	8.623	0.67	
solubility	-	Soluble in water and alcohol but insoluble in acetone and benzene	Soluble in HCL and HNO3 but insoluble in acetic acid and ethanol
%$CaCO_3$ in egg shell	94.6		

It is soluble in water and alcohol but insoluble in acetone and benzene

4.1. Effect of Parameters on Calcium Acetate Preparations

The results for the effects of the parameters are presented in Table 3 below

Table 4 experiment result

Number of experiment	Reaction time (hr)	concentration (M)	Yield (g)	Yield (%
1	1	2	1.2	6
2	1	4	1.6	5.3
3	1	6	1.65	4.12
4	2	2	1.5	7.5
5	2	4	1.57	6.28
6	2	6	1.7	5.66
7	3	2	1.8	8.9
8	3	4	1.9	9.5
9	3	6	2.1	7.86

4.2 Effect of Individual Process Variables

4.2.1. Effect of Reaction Time on the Yield

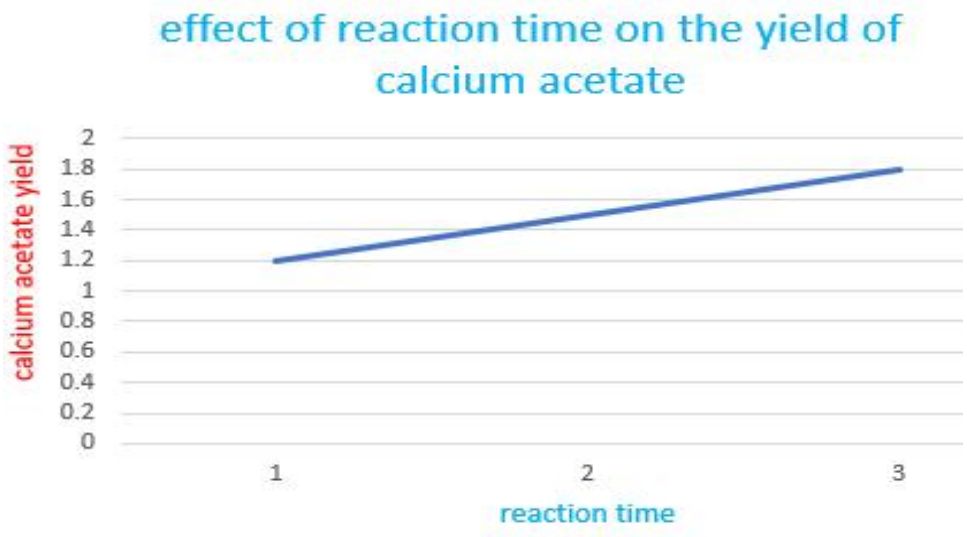
Reaction time was one of the factors that can affect the quantity of the calcium acetate production .

To study the effect of time, the reaction was conducted with specified concentration at 2M.

The average quantity of yield was increased from 1.2 g to 1.8 g, when reaction time was increased from 1 hour to 3 hour.

Table 5:Result for the effect of time

Run	Reaction time(hr)	Concentration (M)	Yield(gm)	Yield(%)
1	1	2	1.2	6
2	2	2	1.5	7.5
3	3	2	1.8	8.9



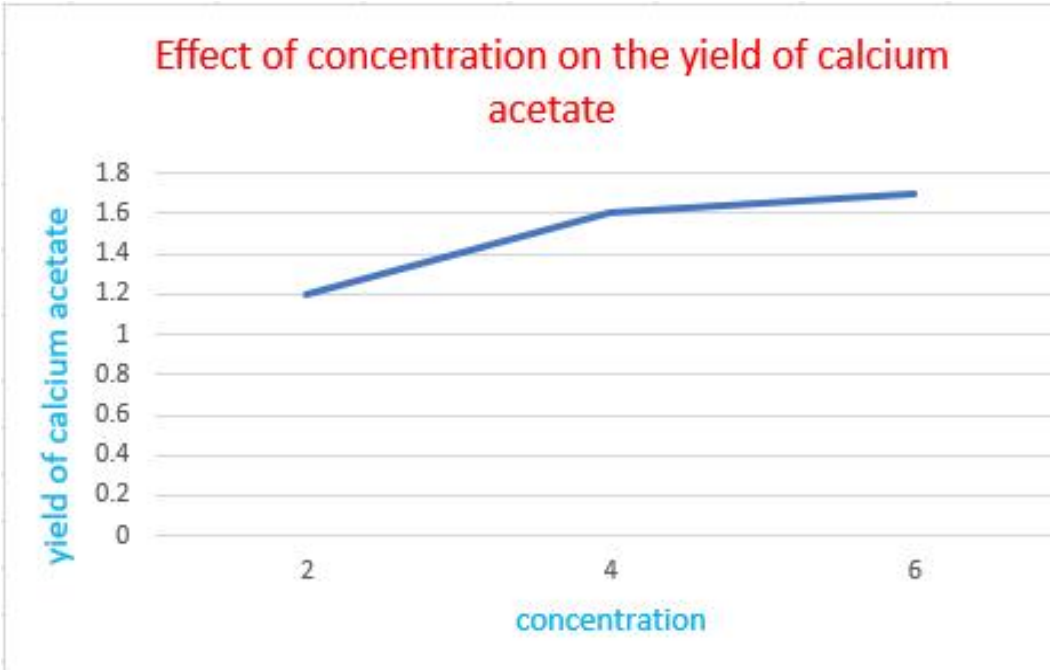
It can be seen from figure above that the yield increases with increasing time. This may be due to an obvious fact. As more time was given for the reaction to take place, more reactants in the solution was interact and more product was formed.

4.2.2. Effect of concentration on the Yield

Another factor that can affect quantity of calcium acetate was concentration. According to the result of the experiment conducted in this study, the quantity of the calcium acetate have been affected by increasing concentration. The average quantity of yield increased from 1.2g to1.7 g, when concentration increased from 2M to 6M..

Table 6:Result for the effect of concentration

Run	Concentration(M)	Reaction time(hr)	Yield(gm)	Yield(%)
1	2	1	1.2	6
2	2	2	1.5	7.5
3	4	1	1.6	5.3
4	4	2	1.62	6.28
5	6	1	1.65	4.12
6	6	2	1.7	5.66

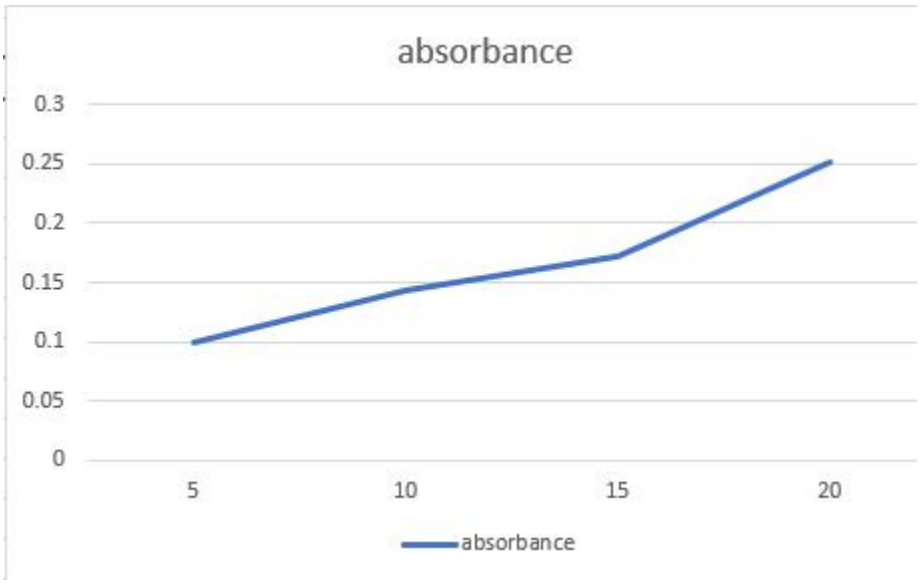

Effect of concentration on the yield of calcium acetate
yield of calcium acetate
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
2
4
6
concentration

The resultsof absorbance summerised in the table below

Table 7:absorbance

Std conc mg/l	5	10	15	20
absorbance	0.099	0.144	0.172	0.252

The result also shown by calibration curve below.



CHAPTER FIVE

5 MATERIAL AND ENERGY BALANCE

5.1. Material Balance

Material balances (also called mass balance) are essential of process design. It is an application of conservation of mass to the analysis of physical system. If it is taken over the complete process, it will determine the quantities of raw materials required and products produced. If it is over individual process units it determines the process stream flows and compositions.

Material balances are also useful tools for the study of plant operation and trouble shooting. They can be used to check performance against design; to extend the often limited data available from the plant instrumentation; to check instrument calibrations; and to locate sources of material loss. To perform the material balance the process steps and parameters should be drawn sequentially, the units of each process stream parameters also be stated properly. The product and byproduct streams are stated as their phase.

Common assumption of “steady state process” is taken for this case. In this project material balance is mainly necessary to perform economic analysis, which enable as for the Material balance can be done on the reactor, filter, evaporator and drying.

General Material balance assumptions:

• 2 shifts per day

• 8 working hours per shift

• 16 working hours per day

• 300 working days per year

• 1,200 tons per year production capacity

PREPARATION OF CALCIUM ACETATE FROM EGG SHELL

• Take1L of water =1kg of water

• Density of acetic acid=1.05g/ml

1,200 tone/year * 1 year/300 days = 4 ton/day **= 4000 kg/day**

From experimental data 50 g of egg shell produce 44g of calcium acetate.

Then 0.05 kg of egg shell →0.0 44kg of calcium acetate

X(?) 4000 kg/day

Mass of egg shell(x) = 4545.5kg of egg shell per day

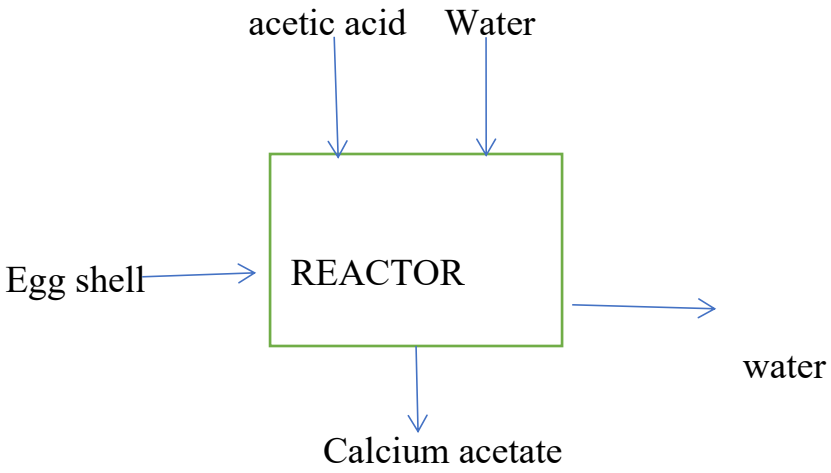
5.1.1 Mass Balance on Reactor

Assuming steady state process will be used, and then generation, accumulation and consumption become zero.

Input+ generation – output-accumulation - consumption = 0

Therefore, input =output

Mass of egg shell + M of water + acetic acid= calcium acetate + water



M acetic acid =Volume * density

=52ml*1.05g/ml

= 54.6g

For 0.05 kg of egg shell 0.0546 kg of acetic acid is needed

4545.5kg of egg shell = x (?)

Mass of acetic acid (x) =4963.7 **kg/day**

For 0.05kg of egg shell 98g of water is needed

4545.5kg of egg shell = x Mass of water (x) =8,909,180kg/day

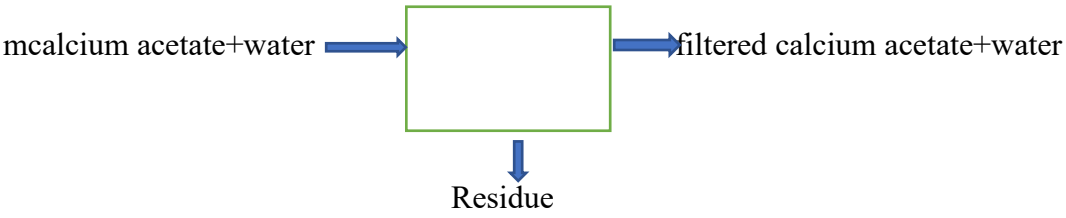
Input = output

m egg shell + m acetic acid +m water=mcalcium acetate+water

4545.5kg+4963.7 kg+8,909,180kg = mcalcium acetate+wate

mcalcium acetate+water =8918689.2kg/day

5.1.2 Mass Balance on filtration



Assuming 1% of the total feed is the unreacted (residue).

Residue=0.01*m calcium acetate+water

= 0.01* 8918689.2

Residue=89186.892kg/day

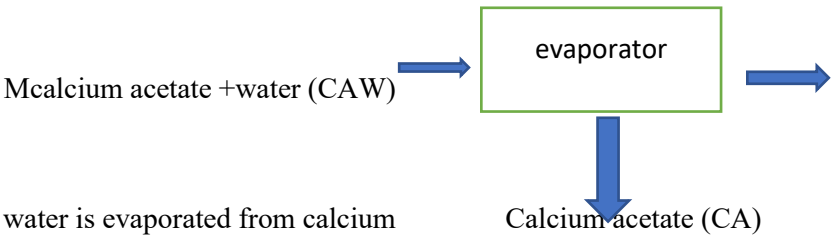
input =output

mCAW=mFCAW +R

8918689.2kg=mFCAW+89186.892kg

mFCAW=8829502.308 kg/day

5.1.3 Material balance on evaporator



Assuming 60% of water is evaporated from calcium acetate.

Input = output

mCAW=mCA+ mW

mCAW = mCA +

0.6mCAW

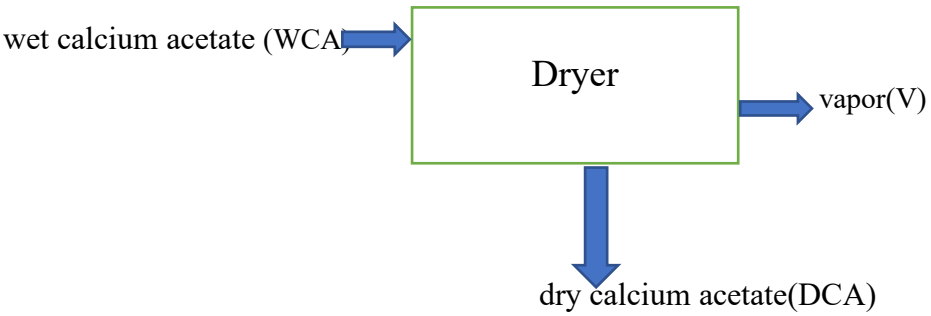
mCA=0.4mCAW

mCA=0.4*8829502.3

mCA= 3531800.9

kg/day

5.1.4 Mass Balance on dryer



Assuming 40% of the total feed is evaporated in dryer.

wet calcium acetate = vapor + dry calcium acetate

mV = 0.4 * mWCA

wet calcium acetate = vapor + dry calcium acetate

mWCA=0.4mWCA+mDCA

mDCA=0.6mWCA

=0.6*3531800.9

mDCA =1412720.4 kg/day

mWCA = 3531800.9

kg/day and

Vapor = 0.4 *3531800.9

= 1412720.36 kg/day

5.2. Energy Balance

Energy balances are also essential for process design to determine the energy requirements of the process: the heating, cooling and power required. In plant operation, an energy balance (energy audit) on the plant will show the pattern of energy usage, and suggest areas for conservation and savings.

The general equation for energy balance can be given as:

Accumulation = Energy out - Energy in + Generation - Consumption

Generally, to determine the cooling or heating requirements of any processing industry simplified equation can be met by ignoring the potential and kinetic energy of the system and considering the inlet and out let enthalpy of the system, heat added or removed from the system. All calculated energy values are the quantity of energy required to run one batch process.

State any assumptions.

– process is operating at steady state

– system does not leak

– system is heterogeneous

– evaporation occurs at 100°C

– vapor is saturated

– shaft work is negligible

– no heat losses

The net change (increase or decrease) in the total energy of the system during a process is equal to the difference between the total energy entering and the total energy leaving the system during that process. That is In chemical processes, the kinetic and potential energy terms are usually small compared with the heat and work terms, and can normally be neglected. But For many processes the work term will be zero, or negligibly small.

5.2.1 Energy Balance on Reactor

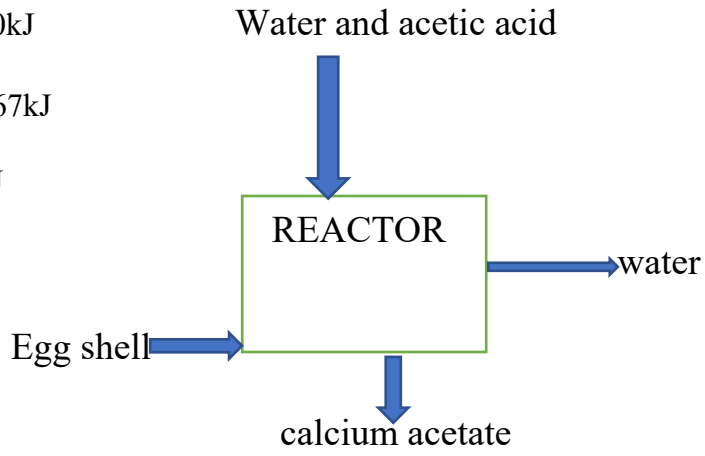
Enthalpy of calcium acetate =1479.5kJ

Enthalpy change of egg shell = 1207.6 kJ

Enthalpy of water = 285820kJ

Enthalpy of acetic acid = 867kJ

Enthalpy of vapor=40.63KJ



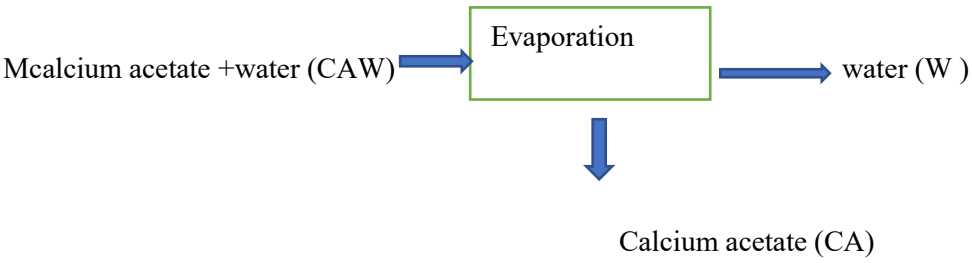
+ **Q=HCA+HW-(HES+HAA+Hw)**

=1479.5KJ+285820KJ-(1207.6kJ+1251.6kJ+867kJ)

=285002.8KJ/day*1day/86400sec

Q=3.3KW

5.2.2 Energy Balance on Evaporator



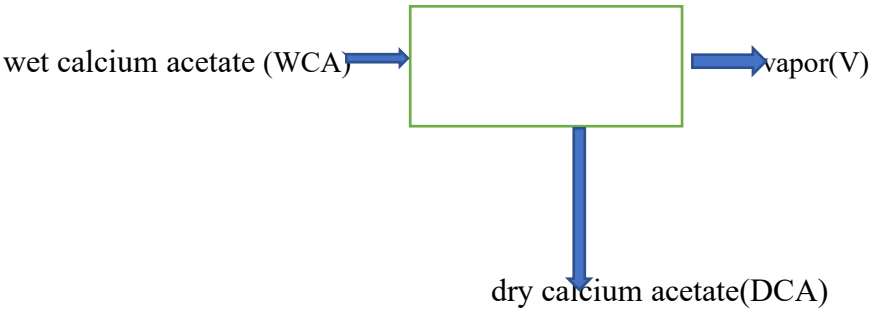
Q=HCA+HW-HCAW

Q=1479.5KJ+285820KJ-(1251.6KJ+1479KJ)

Q=284568.4kg/86400sec

Q=3.2KW

5.2.3 Energy Balance on Dryer



Q=HWCA-(HV+HCA)

Q=1479.5KJ+40.63KJ-(1479.5KJ

Q=2999.63KJ/86400sec=0.034KW

CHAPTER SIX

6. CONCLUSION AND RECOMMENDATION

6.1 Conclusion

In this project two major factors are conducted in the experiment, which affects the quantity of calcium acetate such as concentration, temperature and reaction time. As reaction time increased from 1hr to 2hr and 3hr the yield of calcium acetate was also increased.

On the other hand when the concentration increase from 2M to 6M the quantity of calcium acetate also increased. In this project the maximum effect was achieved at reaction time of 3 hr and at 6M.

In this study, calcium acetate was checked as a possible absorbent for phosphate ion removal. And characterization of calcium carbonate ,calcium acetate and calcium phosphate was done by using physio chemical characterization

6.2 Recommendation

From the experimental outputs obtained from the study on the optimization of calcium acetate production, the following points were recommended:

This experiment was conducted by using only chicken egg shell, hence it is recommended that the coming researcher should use the egg shell of birds and ostriches, shells from beaches and other calcium rich materials

Calcium acetate is imported from other countries.

- Therefore, it is highly advisable to build calcium acetate manufacturing plant in Ethiopia to reduce the imported calcium acetate and environmental pollution.

- The absence of equipment/ devices like X-ray diffraction spectroscopy,vacuum dryer

FTIR machine makes the determination of crucial characteristics, i.e., molecular structure of calcium acetate impossible. Hence, for future studies the department should facilitate the ease of sample characterization.

- Calcium acetate prepared from eggshell should further be studied by future researchers in human trials for the removal of phosphate ion from blood and for the removal of other waster waste water contaminants like nitrate ion, chloride ions. And so forth.

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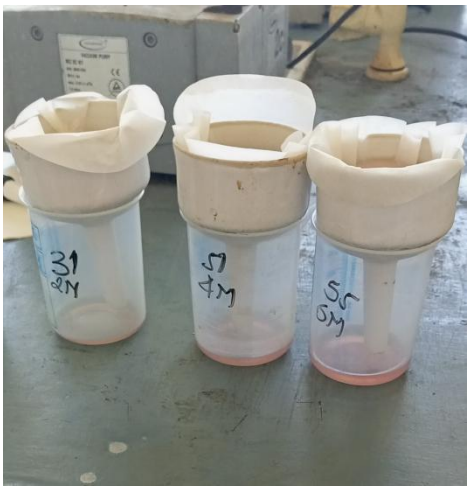
Appendix

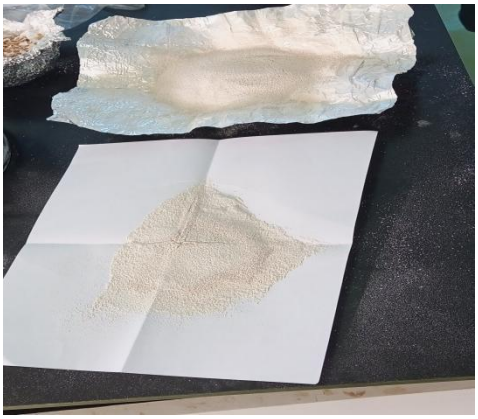
Egg shell sample

Powder of egg shell

Filtration



Powder of calcium acetate



Evaporation

solublity of calcium acetate in water

Solublity of calcium acetate in ethanol