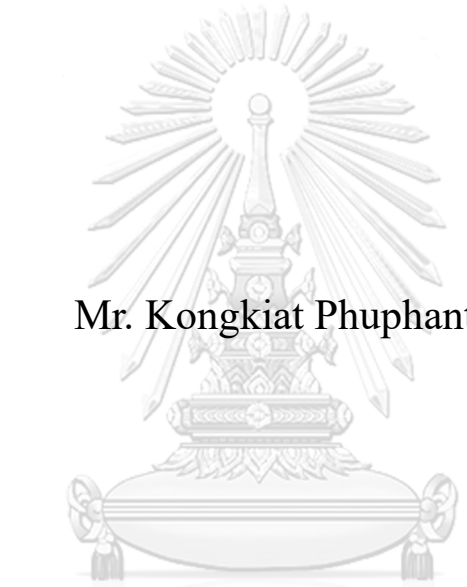
Innovation Process of Amorphous Cellulose - Graphene Oxide Hybrid Structure for Water Treatment in A Shrimp Farm

Mr. Kongkiat Phuphantrakun



A Dissertation Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy in Technopreneurship and
Innovation Management
Inter-Department of Technopreneurship and Innovation Management
GRADUATE SCHOOL
Chulalongkorn University
Academic Year 2022

นวัตกรรมกระบวนการผลิตโครงสร้างเซลลูโลสส่วนอสัณฐานกับกราฟีนออกไซด์สำหรับการบำบัดน้ำในบ่อกุ้ง

นายก้องเกียรติ ภู่พันธ์ตระกูล

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรดุษฎีบัณฑิต
สาขาวิชาธุรกิจเทคโนโลยีและการจัดการนวัตกรรม (สหสาขาวิชา) สหสาขาวิชาธุรกิจเทคโนโลยี
และการจัดการนวัตกรรม
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ปีการศึกษา 2565

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ก้องเกียรติ ภู่พันธ์ตระกูล : นวัตกรรมกระบวนการผลิตโครงสร้างเซลลูโลสส่วนอสัณฐานกับกราฟีนออกไซด์สำหรับการบำบัดน้ำในบ่อกุ้ง. (Innovation Process of Amorphous Cellulose - Graphene Oxide Hybrid Structure for Water Treatment in A Shrimp Farm) อ.ที่ปรึกษาหลัก : ศ. ดร.สนอง เอกสิทธิ์, อ.ที่ปรึกษาร่วม : ศ. กิตติคุณ ดร.อัจฉรา จันทร์ฉาย

วัสดุคอมโพสิตระหว่างเซลลูโลสอสัณฐานและกราฟีนออกไซด์แบบเม็ดเป็นที่นิยมใช้ในการบำบัดน้ำให้บริสุทธิ์ อย่างไรก็ตามวิธีการขึ้นรูปเซลลูโลสอสัณฐานและคอมโพสิตระหว่างเซลลูโลสอสัณฐานกับกราฟีนออกไซด์แบบเม็ดที่มีอยู่นั้นมีความซับซ้อนเพราะต้องใช้สารเคมีหลายชนิด มีขั้นตอนที่ซับซ้อน ใช้ต้นทุนเวลาและพลังงานในการผลิตสูง ในงานวิจัยนี้เราเสนอวิธีการที่มีประสิทธิภาพสำหรับการผลิตเม็ดบีดคอมโพสิตระหว่างเซลลูโลสอสัณฐานกับกราฟีนออกไซด์โดยใช้สารเคมีน้อยลงภายใต้แนวทางที่ไม่ซับซ้อนผ่าน 2 ขั้นตอน ประกอบด้วยกระบวนการเจลาติไนเซชันด้วยกรดซัลฟิวริกเพื่อสังเคราะห์เซลลูโลสที่มีลักษณะเป็นเจลใสโดยใช้กระดาษยูคาลิปตัสเป็นวัตถุดิบตั้งต้นและกระบวนการขึ้นรูปเม็ดบีดโดยใช้เข็มฉีดยาหยดเจลส่วนผสมระหว่างเซลลูโลสและกราฟีนออกไซด์ลงในน้ำที่ปราศจากไอออนเพื่อทำการขึ้นรูปเจลเป็นเม็ดบีด หลังจากกระบวนการขึ้นรูป เซลลูโลสของยูคาลิปตัสที่มีโครงสร้างแบบกึ่งผลึกถูกเปลี่ยนเป็นเซลลูโลสอสัณฐานทำให้ได้รับเม็ดเซลลูโลสอสัณฐาน (เม็ดสีขาว) และเม็ดคอมโพสิตระหว่างเซลลูโลสและกราฟีนออกไซด์ (เม็ดสีน้ำตาลอ่อน) โดยเม็ดบีดทั้งสองแบบมีลักษณะกึ่งทรงกลมที่มีขนาดเส้นผ่านศูนย์กลางเฉลี่ย 2 มิลลิเมตร สีน้ำตาลอ่อนของเม็ดบีดบ่งบอกว่ากราฟีนออกไซด์ถูกฝังอยู่ในเม็ดเซลลูโลสอสัณฐานเรียบร้อยแล้ว และเม็ดบีดตัวอย่างยังได้รับการตรวจวิเคราะห์ด้วยอุปกรณ์ทางวิทยาศาสตร์ประกอบด้วย กล้องจุลทรรศน์อิเล็กตรอนแบบส่องผ่าน เทคนิคฟูเรียร์ทรานส์ฟอร์มอินฟราเรดสเปกโตรสโคปี เทคนิครามานสเปกโทรสโคปี เทคนิคการวิเคราะห์ทางความร้อน และเทคนิควิเคราะห์การเลี้ยวเบนของรังสีเอ็กซ์เรย์ กระบวนการเจลาติไนเซชันและกระบวนการการขึ้นรูปเม็ดบีดในงานวิจัยนี้เป็นวิธีการที่ง่ายและมีประสิทธิภาพในการผลิตเม็ดเซลลูโลสอสัณฐานและเม็ดคอมโพสิตระหว่างเซลลูโลสและกราฟีนออกไซด์ นอกจากนี้วิธีการนี้ยังถูกนำไปเปรียบเทียบกับระบบตัวทำละลายก่อนหน้านี้ในสองมุมมองคือมุมมองของความคุ้มค่าในการผลิตและมุมมองเชิงเศรษฐศาสตร์เพื่อเน้นย้ำถึงข้อดีของวิธีการที่ถูกนำเสนอใหม่ ดังนั้นวิธีการที่เสนอนี้จึงเป็นการผลิตเม็ดบีดคอมโพสิตระหว่างเซลลูโลสอสัณฐานและกราฟีนออกไซด์ที่ใช้งานได้จริง มีประสิทธิภาพ และมีโอกาสในการขยายขนาดการผลิตเพื่อต่อยอดเชิงพาณิชย์ได้ อีกทั้งเม็ดบีดคอมโพสิตระหว่างเซลลูโลสและกราฟีนออกไซด์ยังมีคุณสมบัติเฉพาะตัว คือ สามารถย่อยสลายทางชีวภาพและสามารถนำกลับมาใช้ใหม่ได้ ด้วยคุณสมบัติที่โดดเด่น เม็ดบีดคอมโพสิตจึงถูกพิจารณาเป็นตัวดูดซับที่มีศักยภาพในการรักษาคุณภาพน้ำโดยเฉพาะอย่างยิ่งสำหรับธุรกิจฟาร์มเลี้ยงกุ้งในประเทศไทยและยังถูกพิจารณาเป็นหนึ่งในวัสดุที่เป็นมิตรกับสิ่งแวดล้อมและสามารถประยุกต์ใช้งานได้หลากหลายผลิตภัณฑ์ ในการวางแผนการเพิ่มกำลังการผลิตได้วางแผนเป็นโรงงานทดลองผลิตขนาดเล็กด้วยโดยมีปริมาณการผลิตเจลส่วนผสมระหว่างเซลลูโลสส่วนอสัณฐานและกราฟีนออกไซด์ต่อวันเป็นเกณฑ์ในการแบ่ง และในการวางแผนเชิงพาณิชย์จะเน้นไปที่กลุ่มลูกค้าเกษตรกรที่เลี้ยงกุ้ง งานวิจัยนี้ตอบวัตถุประสงค์ของการวิจัยได้อย่างครบถ้วนทั้ง 4 ข้อ ประกอบด้วย สามารถพัฒนาวิธีการและผลิตภัณฑ์ตัวอย่างเม็ดเซลลูโลสอสัณฐานและเม็ดบีดคอมโพสิตระหว่างเซลลูโลสอสัณฐานกับกราฟีนออกไซด์ได้ สามารถอธิบายลักษณะทางกายภาพและเคมีของตัวอย่างได้ สามารถวางแผนเพิ่มกำลังการผลิตได้ และสามารถวางแผนการขายและแผนการเริ่มต้นธุรกิจได้

สาขาวิชา	ธุรกิจเทคโนโลยีและการจัดการนวัตกรรม (สหสาขาวิชา)	ลายมือชื่อนิสิต .....
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6087756920 : MAJOR TECHNOPRENEURSHIP AND INNOVATION MANAGEMENT
KEYWORD: Cellulose dissolution Amorphous cellulose Cellulose gel Amorphous cellulose-graphene oxide oxide composite Amorphous cellulose-graphene oxide bead
Kongkiat Phuphantrakun : Innovation Process of Amorphous Cellulose - Graphene Oxide Hybrid Structure for Water Treatment in A Shrimp Farm. Advisor: Prof. Dr. SANONG EKGASIT Co-advisor: Prof. Emeritus Dr. Achara Chandrachai

Amorphous cellulose-graphene oxide bead composites are popularly employed in water purification. However, the existing fabrication methods of amorphous cellulose (AC) and amorphous cellulose-graphene oxide (ACGO) beads are complicated with many chemical use, multi-step, time and energy-consuming. In this research, we proposed an efficient method for fabricating amorphous cellulose-graphene oxide (ACGO) beads using less chemical under a simple 2-step approach. The production process of AC and ACGO beads was successfully fabricated via sulfuric acid (H_2SO_4) gelatinization and regeneration using eucalyptus paper as a raw material. The cellulose gel was droplet-extruded into deionized (DI) water and transformed into a solid bead via water regeneration. The semicrystalline eucalyptus cellulose was transformed into amorphous cellulose after the regeneration process. 2 mm in diameter of AC (white beads) and ACGO (light brown beads) quasi-sphere beads were obtained. The light brown colour suggested that graphene oxide (GO) was successfully embedded in AC bead. The embedding of GO in the AC was confirmed by scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FT-IR), Raman spectroscopy (Raman), thermogravimetric analysis (TGA), and X-Ray diffraction analysis (XRD). Gelatinization and regeneration processes provide a simple and efficient method for producing AC and ACGO beads. In addition, the method was compared to previous solvent systems from two perspectives including practical and economic perspectives to emphasize the advantages of the proposed method. Hence, this proposed method was the practical, efficient, and scalable fabrication of ACGO for commercialization. Moreover, the biodegradable, and renewable ACGO is a potential adsorbent for sustaining water quality, especially for shrimp farms and the ACGO bead can also be considered as one of the alternative “Green materials” for various applications. In the stage of planning for scaling-up scale consists of two scales which are pilot and near commercialization scale. The quantity of ACGO gel is the criteria factor separated between the two scaling-up scales. The quantity of ACGO gel of pilot and near commercialization scales are 510 and 2,550 L per day, respectively. The commercialization plan aims to Thai shrimp farmers to be target customer. Therefore, this research answers all 4 research objectives. Firstly, the ACGO bead fabrication protocol and prototype beads are implemented. Secondly, the prototype beads are characterized via technical tools. Thirdly, the scaling-up plan is created and lastly the commercialization plan and launching plan are employed in many perspectives and scenarios.

Field of Study:	Technopreneurship and Innovation Management	Student's Signature .....
Academic Year:	2022	Advisor's Signature .....
		Co-advisor's Signature .....

ACKNOWLEDGEMENTS

I would like to thank my dissertation adviser Professor Dr. Sanong Ekgasit and Professor Emeritus Dr. Achara Chandrachai for their advice and support during my Ph.D life as well as patiently practices my science skill and social science knowledge after science skill within the whole research.

I would like to thank Associate Professor Dr. Chatchawan Chaisuekul, Professor Dr. Chavalit Ratanatamskul, Professor Dr. Tawatchai Charinpanitkul, and Associate Professor Dr. Warunee Ariyawiriyanan for serving as chairman and members of thesis committee, respectively, for useful suggestions, valuable discussions, and helpful comments.

Above all, I gratefully acknowledge the Ratchadapisek Somphot Fund (Chulalongkorn University) and the Research Network NANOTEC (RNN) program of the National Nanotechnology Center (NANOTEC), NSTDA, Ministry of Higher Education, Science, Research and Innovation, Thailand.

Kongkiat Phuphantrakun

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List of Abbreviations

AC.....activated carbon

ACGOHS.....amorphous cellulose-graphene oxide hybrid structure

ACGO….....amorphous cellulose-graphene oxide

AG.....silver

AMOX.....amoxicillin

AOPs.....advanced oxidation processes

APTES.....(3-Aminopropyl)iethoxysilane

AS.....arsenic

BC.....bacteria cellulose

BET.....Brunauer-Emmett-Teller

BJH.....Barrett-Joyner-Halenda

CAP.....chloramphenicol

Cd.....cadmium

CEF.....ceftriaxone

CFX.....cefalexin

CIP.....ciprofloxacin

CM.....clarithromycin

CNFs.....cellulose nanofibers

Cr.....chromium

CTC.....chlortetracycline

CN.....cyanida

CNC.....cellulose nanocrystal

CNT.....carbon nanotube

Co.....cobalt

CrO_4^{-2}.....dioxido(dioxo)chromium (chromate)

Cu.....copper

CZ.....cefazolin

DFT.....density functional theory

DMAC.....LiCl/N,N-dimethylacetamide

List of Abbreviation (continued)

DMSO.....dimethyl sulfoxide

DOEs.....design of experiments

DWTPS.....drinking water treatment plants

DX.....dicloxacillin

DP…….depreciation

DXC.....doxycline

EMIMAc.....ethyl-3-methylimidazolium

EmimOAc.....1-ethyl-3-methylimidazolium acetate ionic liquid

ENR.....enrofloxacin

EPTMAC.....glycidyl trimethylammonium

ERY.....erythromycin

Fe.....iron

Fe_3O_4.....iron oxide

FF.....florfenicol

FTIR.....fourier transform infrared spectroscopy

GO.....graphene oxide

HCl.....hydrochloric

Hg.....mercury

HPAMAM .....hyperbranched poly(amidoamine)

H_3PO_4.....phosphoric acid

HNO_3.....nitric acid

H_2SO_4.....sulfuric acid

LCA.....life cycle assessment

LiCl.....lithium chloride

LOM.....lomefloxacin

MB.....methylene blue

MD.....metronidazole

MFC.....cellulose microfibril

MGCNF.....magnetic cellulose nanofiber

List of Abbreviation (continued)

Mn.....manganese

MPs.....microplastics

NaCl.....sodium chloride

NaOH.....sodium hydroxide

NCC.....nanocrystalline cellulose

NH^{4+}.....ammonium

Ni.....nickle

NMMO.....N-methyl morpholine-N-oxide

NOR.....norfloxacin

NPD.....new product development process

NPs.....nanoplastics

OFL.....ofloxacin

OR.....operation research

OTC.....oxytetracycline

Pb.....lead

PC.....piperacillin

PEI.....poly(ethyleneimine)

PNG.....penicillin G

Raman.....raman spectra

REM.....roxithromycin

RGO.....reduced graphene oxide

RO.....reverse osmosis

RC.....regenerated cellulose

RCM.....regenerated cellulose microsphere

SAR.....sarafloxacin

SD .....sulfadiazine

SEM.....scanning electron microscope

SMX .....sulfamethoxazole

SMZ .....sulfamethazine

List of Abbreviation (continued)

SP.....sulfapyridine

SQ.....sulfaquinoxaline

TAP.....thiampheicol

TC.....tetracycline

TEM.....transmission electron microscopy

TSR.....Thiensurat PLC.

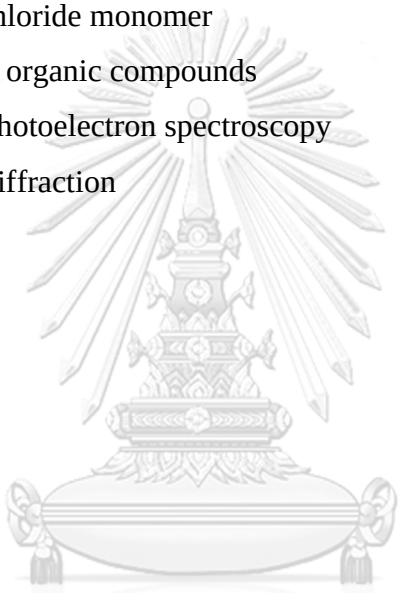
VCM.....vinyl chloride monomer

VOCs.....volatile organic compounds

XPS.....x-ray photoelectron spectroscopy

XRD.....x-ray diffraction

Zn.....zinc



List of Symbols

kg.....kilogram

m.....million

m^2.....square meter

m^3.....cubic meter

µg/g……..…microgram per gram

mg/g.....milligram per gram

q_e.....adsorbed amount

µg/L.....microgram per liter

mL……..…… milliliter

L .....liter

%.....percent

%R.....removal percentage

%v/v……..…...%volume per volume

%wt.....percent weight by weight

%w/v.....percent weight by volume

%w/w.....percent weight by weight

$.....dollar

Chapter 1
Introduction

1.1 Rational of the study

Water contaminants are current issues urgency to be solved because they affect human health and water ecosystem. Those contaminants consist of heavy metals, microplastics, pesticides, antibiotics, dyes, bacteria and volatile organic compounds (VOCs), among others. Activated carbon (AC), carbon nanotube (CNT) and zeolite-based materials are applicable to be absorbents, but the contaminants are still detected in water sources [1].

Water contaminants cause headaches, fatigue, skin problems, nausea, eye, nose and throat irritation, breathing problems, etc. Furthermore, some VOCs and pesticides suspected cause of cancers and deaths [2].

Diseases caused from contaminated drinking water are divided into three main diseases: bacterial disease, viral disease, and parasitic disease. Diarrhea is an example of bacterial disease. Campylobacter jejuni is the bacteria that causes approximately 4 to 15% of diarrhea worldwide. Contaminated drinking water also causes other symptoms such as nausea, vomiting, dehydration and renal failure. Viral diseases, on the other hand, such as hepatitis, cause jaundice, fatigue, loss of appetite, discomfort, and high fever. In the worst-case scenario, a virus-infected person could become infected with bacteria, which could lead to death. Other common viral diseases include encephalitis, poliomyelitis, and gastroenteritis. Drinking contaminated water may also expose a person to parasitic diseases such as cryptosporidiosis, galloping amoeba, and giardiasis [2].

Another water contaminants are microplastics (MPs) and nanoplastics (NPs) which are synthetic polymers that are nonbiodegradable. Accumulation of these contaminants has detrimental effects to one's health. MPs and NPs enter the human body through direct and indirect channels. MPs in drinking water, especially those with less than 10 μm size, were detected in drinking water treatment plants (DWTPS). The result confirmed that there were more than 4,000 contaminants per liter in treated water [3]. A study was also conducted to test MPs from 259 water bottles (258 single-

use plastic bottles and one glass bottle). The samples were collected from 19 locations in 9 countries (China, USA, Brazil, India, Indonesia, Mexico, Lebanon, Thailand, and Germany) and included 11 brands of bottled water. The study showed that 242 bottles, or 93.4 percent of the samples, were contaminated [4]. Microplastics in tap water were also investigated, with 159 samples collected from Cuba (1), Ecuador (24), England (3), France (1), Germany (2), India (17), Indonesia (21), Ireland (1), Italy (1), Lebanon (16), Slovakia (8), Switzerland (2), Uganda (26), and the United States (36) being studied. The findings revealed that there were 0 - 61 contaminated particles per liter, with an average of 5.45 particles per liter [4].

Volatile organic compounds (VOCs) are released into the atmosphere by chemical industries, agricultural sections, fuel refineries, and pharmaceutical plants and nay end up in the water ecosystem [5]. Water samples from the Chao-Phraya river were tested, and the results revealed that vinyl chloride monomer (VCM), a recognized human carcinogen and highly hazardous organic compound, was present in high concentrations (338 g/L). This level of VCM will be not accepted by equivalent plants in the United States of America. Not only VCM, but also other VOCs, as well as antioxidants found in plastics, were detected. The remaining chlorinated compounds found in the samples are chloroform (1 g/L), 1,1-dichloroethane (5 g/L), and 1,2-dichloroethane (10 g/L). Other VOCs found in the samples included phthalate esters, phenols, oxygenated compounds, and aliphatic hydrocarbons. Heavy metals including arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), and zinc (Zn) were also detected from the samples [6]. Furthermore, VOCs are hazardous chemicals that contribute to pollution and reduce air quality. Various aromatic, aliphatic, alcoholic, carbonyl, and chlorinated VOCs were all detected in the air [7].

Antibiotics are substances that are used in animals as feed additives to promote growth. They are also used to protect humans against microbial diseases. The hospital effluent contained antibiotics such as Ciprofloxacin, Cephalexin, and β-lactams. Tetracyclines and Macrolides were also found in culture wastewater [8]. Pesticides are also major contaminants in the aquatic ecosystem, affecting both the environment and human health. Nine pesticides were detected in water samples from Thailand's main rivers, including aldrin, alpha-BHC, DDT, dieldrin, heptachlor, lindane, methyl

parathion, dimethoate, and diazinon [9]. Without an effective water treatment system, the aforementioned water contaminants such as heavy metals, anions, dyes, antibiotics, pesticides, MPs and BPs, and VOCs could have long-term effects on humans and the environment.

Adsorption is one of the most effective methodologies for treating water before it is discharged into a water source since because of its high efficiency, low cost, easy regeneration and operation, mass scale production, and accessibility [8]. Adsorption capacity is affected by adsorbent properties such as surface area, temperature, and pressure. Currently, activated carbon (AC), the primary adsorbent used to treat pollutants, is inefficient in treating target contaminants. As a result, alternative adsorbents must be studied and implemented to replace environmentally unfriendly adsorbents [7]. Conventional methods for treating contaminated water, which mostly used activated carbon as an adsorbent, are being questioned for their efficacy. β - Lactams (17 - 43%), Macrolides (40 - 46%), Sulfonamides (20 - 24%), and Tetracyclines (66 - 90%) could be treated using traditional methods. Furthermore, while advanced oxidation processes (AOPs) and membrane filtration had high removal efficiency, those methods were complicated and expensive [8].

Activated carbon, carbon nanotubes, biochar, ceramic, zeolite, and other adsorbent materials are currently available to adsorb water contaminants. Activated carbon is a popular adsorbent material that has a high adsorption efficiency but is not environmentally friendly [1].

Table 1.1 Environmental perspectives of adsorbents [1]

Material	Biocompatibility	Biodegradable	Renewable
Cellulose -nanofibers (CNFs)	High	High	High
Graphene oxide	Medium	Medium	High
Activated carbon	Low	Medium	Medium

Activated carbon would cause environmental issues and have an impact on human life in the long run because of its high cost and energy consumption in the manufacturing and regeneration processes [1].

Cellulose is an environmentally friendly alternative material. Because of its biodegradability, renewability, nontoxicity, and biocompatibility, cellulose is gaining popularity as a material for environmentally friendly and safe products. Indeed, cellulose is now used in a variety of commercial products due to its environmentally friendly and unique properties. Cellulose extracted from Borojo fruit coated with poly(ethyleneimine) (PEI) could capture up to 98% of hexanal vapors [5]. Furthermore, cellulose's adsorption capacity could be increased by combining it with other substances such as graphene oxide, carbon nanotubes, activated carbon, and so on [1].

Table 1.2 Adsorbent types and water contaminants [1]

Adsorbent	Contaminants
Activated carbon-based material, cellulose-based material, graphene-based material, etc.	Microplastics and nanoplastics (MPs and NPs), volatile organic compounds (VOCs), antibiotics, pesticides, heavy metals, anions, dyes, etc.

Sulfonation and TEMPO-mediated oxidation were the two main chemical approaches used to produce nanocelluloses. However, existing cellulose manufacturing processes are costly and complicated, resulting in high-priced final products [1]. As a result, developing a new technology to produce amorphous cellulose is a difficult task.

Currently, various technologies are being used to obtain nanocellulose, each with its own set of advantages and disadvantages. However, the main issues with these technologies are not efficiency and cost. The total cost of an initial through an end process, including recycling, remains high. Furthermore, activated carbon, an existing adsorbent, is less efficient and more expensive to produce [1]. To overcome these constraints, the researcher would like to use a new technology to create an amorphous cellulose-graphene oxide hybrid structure that can be used as an alternative adsorbent for water and air remediation.

Scaling up processes will be implemented after the ACGO bead production process has been implemented in the laboratory. Another challenge is the complexity

of scaling up from laboratory scale to pilot scale and then to near commercial scale of the ACGO bead because the success of the scaling up process is dependent on many factors such as the proportion of input material, temperature, pressure, acid and alkalinity, and plant design, among others [10]. Furthermore, scientific and engineering knowledge is a critical tool for implementing a large-scale manufacturing plan. The scale-up procedure must be implemented during the initial phase of the scaling-up process. The scale-up procedure was divided into five steps: developing a lab protocol, designing a simple plant flow diagram, separating scale-up of each process step, linking process steps, and performing a life cycle assessment (LCA) [10]. All related parameters would be monitored throughout the entire production process in order to achieve ACGO bead standard quality. The scaling up of a paste-glue product was studied, with the original amount starting from 1,000 mL reactor to 500 L reactor and expanding to 1,500 L by monitoring all parameters [11].

Therefore, three challenge parts of this research must be studied: the innovative methodology process for ACGO bead production, the ACGO bead scaling-up and the commercialization plan.

1.2 Research question

1) How to develop process of AC and ACGO bead fabrication ?
2) How to characterize the AC and ACGO bead ?
3) How to create a scaling-up production plan ?
4) How to create commercialization and launching plan ?

1.3 Research objective

1) To develop process of AC and ACGO bead fabrication
2) To characterize the AC and ACGO bead
3) To create a scaling-up production plan
4) To create commercialization and launching plan

1.4 Research framework

Table 1.3 Research framework

Phase	Objective	Method	Outcome
1. Study existing ACGO bead manufacturing, IP surveys, and production designs	To study and develop innovative process to produce the ACGO bead	Qualitative approach	Innovative methodology of ACGO bead fabrication
2. Develop the ACGO bead prototype and validate the product	To develop the ACGO bead prototype through new innovative process and validate the product	Experiment design and quantitative approach	ACGO bead and characterization
3. Develop mass scale production process	To apply the design of experiments (DOEs) for mass scale production process	Qualitative approach	A scaling-up production plan
4. Implement commercialization plan	To commercialize and launching plan	Qualitative quantitative approach	Commercialization plan

The research is divided into four phases as following:

Phase 1: This phase studies about existing ACGO bead manufacturing, IP surveys and production designs

Phase 2: The ACGO bead production consists of two stages including developing the amorphous cellulose and the ACGO bead. After that, the validation of the product will be processed

Phase 3: This phase is to implement mass scale production plan

Phase 4: This phase is to implement commercialization plan

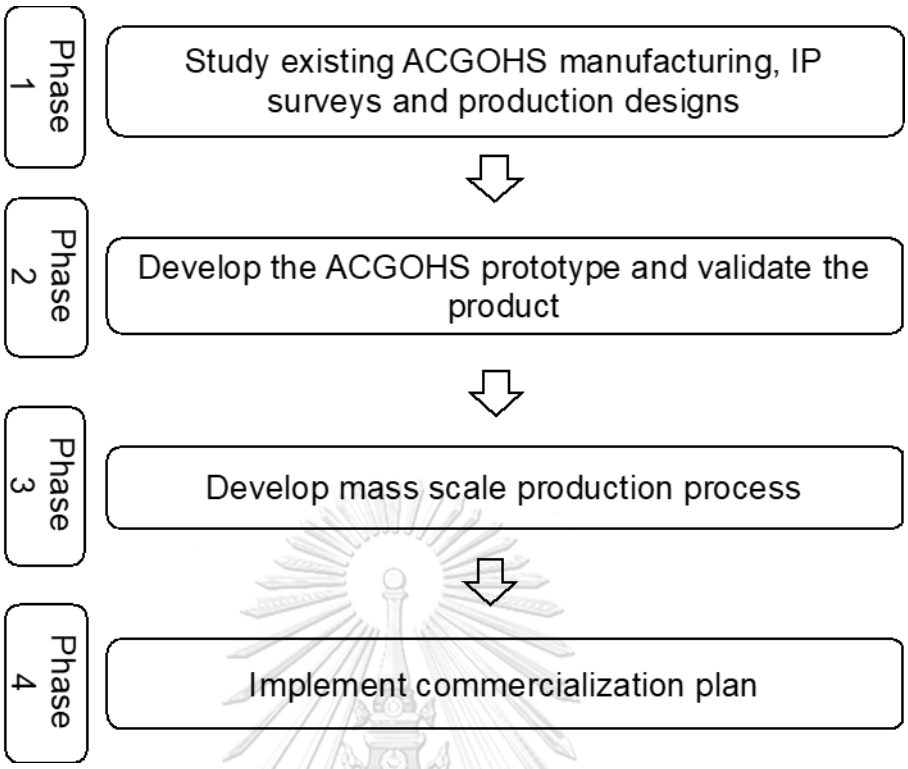


Figure 1.1 Research methodology diagram

1.5 Scope of study

1) The ACGO composite was fabricated only in the bead-form
2) The target is only Thai shrimp farming industry

1.6 Expected benefit

1) Academic contribution: The innovative process for the fabrication of ACGO bead
2) Practical contribution: The AC and ACGO beads

1.7 Research timeline

The dissertation started from January 2021 and finished by March 2023, approximately 27 months. A milestone of each stage is set as Table 1.4.

Table 1.4 Research timeline

Process	Year 2021												Year 2022												Year 2023		
	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
Study existing ACGOHS manufacturing, IP surveys and production designs	■	■	■	■																							
Develop the ACGOHS prototype and validate the product					■	■	■	■	■	■	■	■															
Develop mass scale production plan													■	■	■	■	■	■	■	■							
Implement commercialization and launching plan																					■	■	■	■	■	■	■

Chapter 2
Literature review

2.1 Water treatment methodology

There are four major wastewater treatment processes: physical unit operation, chemical unit process, biological unit process, and physicochemical unit process [12].

Physical unit operations are methods of wastewater treatment that employ forces to separate dissolved solids from water. The majority of these methodologies are in the preliminary treatment process. Screening, comminution, skimming, mixing, floatation, sedimentation, centrifugation, filtration, grit removal, and other processes are examples of these. To have a reaction for separating substances from wastewater, chemical substances must be mixed with wastewater. These processes include precipitation, neutralization, disinfection, and so on. The biological unit process requires microorganisms to digest or convert organic substances into gas, which may increase the number of microorganisms. These include activated sludge, trickling filters, aerated lagoons, anaerobic filters, anaerobic ponds, stabilization ponds, and so on. To get rid of organic and inorganic substances that dissolve in water, the physicochemical unit process requires both physical and chemical processes to work together. Ion exchange, carbon adsorption, reverse osmosis, electrodialysis, and other processes are examples of these [12].

Table 2.1 Treatment methodology

Treatment methodology	Methodology
Physical unit operation	screening, comminution, skimming, mixing, floatation, sedimentation, centrifugation, filtration, grit removal
Chemical unit process	precipitation, neutralization, disinfection
Biological unit process	activated sludge, trickling filter, aerated lagoon, anaerobic filter, anaerobic pond, stabilization pond
Physicochemical unit process	ion exchange, carbon adsorption, reverse osmosis, electrodialysis

The water treatment process could be divided into 4 phases which are preliminary treatment, primary treatment, secondary treatment and tertiary treatment [12]. Screening, sedimentation, floatation, and other early stages of wastewater treatment are examples of preliminary treatment. Primary treatment is the process of separating sediment from wastewater, which includes screening and sedimentation. Secondary treatment is the stage in which organic substances and sediment are separated and removed from wastewater. The majority of processes are biological in nature.

Tertiary treatment is the stage in which the remaining organic substances and sediment from secondary treatment are separated and eliminated. This stage is dependent on the desired water quality. The physicochemical unit process is currently in the tertiary treatment phase. It is used to remove organic and inorganic substances from wastewater. Carbon adsorption, ion exchange, ultrafiltration, reverse osmosis, electrodialysis, and other physicochemical unit processes are examples. The goal of this process is to obtain the expected quality of water, which is usually of high standard. Carbon adsorption is used to separate sediment. Ion exchange is used to exchange the charge of contaminants such as NH_4^+, Cu^{2+}, CrO_4^{-2}, Zn^{2+}, Ni^{2+}, and others. Ion exchange requires the use of chemicals such as NaCl, HCl, H_2SO_4, NaOH, and others as reactors. A porous membrane capable of dissolving sediments and very small sediments is required for ultrafiltration. Reverse osmosis (RO) is well-known for separating dissolved salts by using a semipermeable membrane as a filter at a higher pressure than osmotic pressure. This method yields high-quality drinking water.

To separate salt from sea water, electrodialysis is commonly used. It is suitable for nitrogen and phosphorus removal. It is the final step in the water treatment process in an industrial factory. The system is composed of permeable membranes with positive and negative charges [12]. Adsorption is regarded as the most efficient and worthwhile physicochemical unit process. In a study comparing reverse osmosis and adsorption from wastewater in Saudi Arabia, the Saudi bentonite clay had a higher removal efficiency than the reverse osmosis (RO) process (88.89% to 87.92%). Furthermore, the Saudi bentonite clay costs 0.134 US dollar per kg, whereas the reverse osmosis module costs $2,666 per membrane module [6].

2.2 Adsorption capacity of various adsorbents

Various data on the adsorption capacity of various adsorbents, including activated carbon-based material, biochar, graphene-based material, cellulose-based material, and cellulose-graphene oxide hybrid structure, were gathered and presented in Table 2.2. Accordingly, cellulose-GO-based adsorbents have a higher adsorption capacity than activated carbon-based adsorbents. The adsorption capacity of cellulose-GO-based adsorbents to tetracycline (TC), amoxicillin (AMOX), norfloxacin (NOR), ciprofloxacin (CIP), ofloxacin (OFL), oxytetracycline (OTC), erythromycin (ERY), and penicillin G (PNG) was greater than that of activated carbon and biochar. It implies that if the cost of producing ACGOHS was lower or the same as the cost of producing activated carbon, ACGOHS could be an alternative material adsorbent to replace the AC.

For heavy metal removal, cellulose-GO-based absorbents outperform AC-based adsorbents in the removal of methylene blue (MB), humic acid, arsenic, cadmium, chromium, copper, lead, silver, and zinc. Rhodamine B has nearly the same adsorption capacity. Some absorption capacities, such as barium, iron, manganese, mercury, nitrogen, phenol, selenium, sulphate, fluorine, aluminum, alkylbenzene sulfonate, cyanide (CN), coliform, E.coli, and disease-causing bacteria, could not be compared because additional information was required.

As a result of the existing data, it can be concluded that cellulose-GO-based absorbents have a higher adsorption capacity than activated carbon-based adsorbents because, while some parameters were not compared, none of them showed that the adsorption capacity of cellulose-GO-based adsorbent is lower than that of activated carbon-based adsorbent.

Table 2.2 Adsorption capacity of various adsorbents

Material	Material form	Contaminant	Adsorption capacity (mg/g)	Ref.
Activated carbon-based material (AC)	Native AC	As(V)	0.03 - 43.60	[13]
		Pb^{2+}	1.66-388.86,66.23	[13],[14]
		Cr (VI)	3.46	[14]
		Tetracycline (TC)	58.82	[14]
		Naphthalene	111.79	[14]

Table 2.2 Adsorption capacity of various adsorbents (continued)

Material	Material form	Contaminant	Adsorption capacity (mg/g)	Ref.
Activated carbon-based material (AC)	Native AC	Paracetamol	255	[14]
		Iopamidol	147	[14]
		Humic acid	6.24	[14]
		Phenol	1.51	[14]
	Cellulose bead with magnetic nanopaticles and AC	Zn	20.80	[14]
	Impregnation modified AC	Humic acid	9.06	[14]
	Modified AC	Cd(II)	1.98	[14]
		Pb^{2+}	95.24	[14]
		MB	62.50	[14]
		Cr (VI)	18.52	[14]
		Amoxicillin (AMOX)	57	[14]
		TC	455.80	[14]
		Naphthalene	125.22-131.20	[14]
		Paracetamol	514	[14]
		Iopamidol	1050	[14]
		Ar(V)	27.78	[14]
		Ceftazidime	161.3-200	[14]
		Phenol	3.153-3.546	[14]
	Silver ions onto AC	Ag^{+}	59.52	[15]
	Powdered activated carbon (PAC)	Norfloxacin (NOR)	124	[16]
		Ciprofloxacin monohydrochloride (CIP)	127	[16]
		Lomefloxacin hydrochloride (LOM)	190	[16]
		Sarafloxacin hydrochloride (SAR)	120	[16]
		Enrofloxacin (ENR)	93.5	[16]
		Ofloxacin (OFL)	104	[16]
		CIP	20-418.41	[17]
		NOR	31.93-638.66	[17]
		TC	20-1121	[17]
		Oxytetracycline (OTC)	308-649.40	[17]
		AMOX	20-570.40	[14]
		Peniciln G (PNG)	8.41	[14]

Table 2.2 Adsorption capacity of various adsorbents (continued)

Material	Material form	Contaminant	Adsorption capacity (mg/g)	Ref.
Biochar		Ofloxacin (OFL)	180 µg/g	[8]
		Sulfadiazine (SD)	200 µg/g	[8]
		Sulfamethoxazole (SMX)	200 µg/g	[8]
		Sulfamethazine (SMZ)	195 µg/g	[8]
		Cefalexin (CFX)	205 µg/g	[8]
		AMOX	195 µg/g	[8]
		TC	195 µg/g	[8]
		TC	350	[18]
		SMZ	12	[18]
		NOR	290	[18]
		Erythromycin (ERY)	160	[18]
		Chloramphenicol (CAP)	17	[18]
		OTC	263.80	[19]
Graphene-based material	GO and manganese oxide NPs	Pb	553.00	[14]
	GO hydrogel	Rhodamine B	29.44	[14]
	GO/chitosan hydrogel	Cu(II)	70.00	
		Pb(II)	90	[14]
		MB	> 300.00	[14]
	Polydopamine/GO hydrogel	Pb(II)	336.32	[14]
		Cu(II)	145.48	[14]
		Rhodamine B	207.06	[14]
	Graphene/CNT aerogel	MB	81.97	[14]
	Graphene	As (V)	5.21	[14]
	Hydrogel	MB	7.85	[14]
	Ethylene diamine modified GO	Ibuprofen	95.20	[14]
	Nitrogen-containing GO adsorbents for cationic heavy metals	As (V)	35.50 - 104.13	[14]
		Cd	181.00 - 435.85	[20]
		Cr (VI)	166.98 – 625.00	[20]
		Hg	374.00	[20]
	Oxygen-containing GO adsorbents	Cu	23.04 - 432.90	[20]
		Zn	121.70 - 251.58	[20]

Table 2.2 Adsorption capacity of various adsorbents (continued)

Material	Material form	Contaminant	Adsorption capacity (mg/g)	Ref.
Graphene-based material	Oxygen-containing GO adsorbents for cationic heavy metals	Ag^{+}	142.20	[14]
		Cd	45.05 - 232.36	[20]
	Sulfydryal modified GO/chitosan composite	Cd	177.00	[14]
		Pb	447.00	[14]
		Cu	425	[14]
	Surfactant modified graphene	Cu	369.16	[14]
		Mn	223.67	[14]
	Graphene	OFL	200 µg/g	[8]
		SD	180 µg/g	[8]
		SMX	175 µg/g	[8]
		SMZ	190 µg/g	[8]
		CFX	200 µg/g	[8]
		AMOX	196 µg/g	[8]
		TC	200 µµg/g	[8]
Cellulose-based material	Spherical cellulose (Beads)-SCAM-1	Cu^{2+}	83.56	[21]
	Cellulose beads (Iron oxyhydroxide)	Arsenate	33.2,99.60	[21]
	Composite material with sodium montmorillonite (NaMMT)	Cr (VI)	22.20	[21]
	Composite material, lignocellulose adsorption medium	Asenate	32.80	[21]
	Magnetic hybrid hydrogels	Cu^{2+}	45	[21]
		Fe^{2+}	94	[21]
		Pb^{2+}	28	[21]
	Xanthated banana nanocellulose	Cd(II)		[21]
	CNC-COOH (TEMPO)	MB	769.00	[22]
	CNC-SO_3-	MB	118.00	[22]
	CNFs	As (V)	25.50	[22]
	CNF-COOH (TEMPO)	Cr (III)	58.00	[22]
		Zn^{2+}	67.00	[22]

Table 2.2 Adsorption capacity of various adsorbents (continued)

Material	Material form	Contaminant	Adsorption capacity (mg/g)	Ref.
Cellulose-based material	CNF-CMC, crosslinked using butanetetracaboxylic acid	Ag^{+}	106.00	[22]
		Hg	131.40	[22]
		Pb^{2+}	111.50	[22]
	CNC-PO_4^{2-} (phosphorylation of CNC)	Ag^{+}	136	[22]
		Cu^{2+}	117	[22]
		Fe^{3+}	115	[22]
	Microcrystalline cellulose	AMOX	12.58-87.70	[23]
		Ampicillin monohydrate	9.79-19.22	[23]
Cellulose-graphene oxide hybrid structure	GO/CNF hybrid monolith	MB	151.51-227.27	[24]
	Nanocellulose:GO mass ratio : 7:3, hybrid aerogel	MB	256.60	[25]
	GO/CNFs hybrid aerogel	Doxycline (DXC)	469.74	[26]
		Chlortetracycline (CTC)	396.49	[26]
		OTC	386.53	[26]
		TC	343.84	[26]
	GO/CNFs hybrid aerogel	CIP	421	[27]
		Florfenicol (FF)	419	[27]
		Roxithromycin (REM)	308	[27]
		ERY	292	[27]
		NOR	135	[27]
		OFL	128	[27]
		Thiamphenicol (TAP)	431	[27]
		PNG	475	[27]
		CFX	382	[27]
		AMOX	231	[27]
		Sulfaquinoxaline (SQ)	239	[27]
		SD	229	[27]
		Sulfamerazine (SM)	328	[27]
		Sulfapyridine (SP)	227	[27]
		SMZ	303	[27]
		SMX	220	[27]

Table 2.2 Adsorption capacity of various adsorbents (continued)

Material	Material form	Contaminant	Adsorption capacity (mg/g)	Ref.
Cellulose-graphene oxide hybrid structure		DXC	501	[27]
		CTC	479	[27]
		OTC	487	[27]
		TC	455	[27]

ACGO consists of hydroxyl, carboxyl, and other functional groups, which are determinants in the removal of cations. However, the presence of these groups makes the surface anionic properties of ACGO suitable for metal retention. By the way, electrostatic interactions would repel anionic ions such as the case of nitrates and nitrite. So, Cellulose-based adsorbents are required to increase the retention capacity of the negatively charged substances and improve selectivity. The surface modification of cellulose for use in the treatment of water contaminated with anion has been modified using quaternization with nitrogen salts. The nitrogen salts for the quaternization of bio-adsorbents, e.g. N,N-dimethylformamide, 2,3 Epoxypropyl trimethyl ammonium chloride, methyl trimethyl ammonium bromide, and epichlorohydrin. Recently, Rodrigo Ortega-Toro et al. proposed water treatment alternatives such as nitrate and phosphate adsorption using cellulose extracted from corn stems and biochar by quaternized cellulose modified with cetyltrimethylammonium chloride [28]. To increase ACGO capacity to retain anionic ions (nitrite and nitrate) and improve their selectivity of ACGO, we can modify ACGO surface by quaternized with cetyltrimethylammonium chloride. The etherification reaction is carried out by reacting a quaternary ammonium salt with the centers at the cellulose structure, resulting in a positively charged adsorbent. Therefore, the modified ACGO with a positive charge (cation) has the potential to absorb a negative charge (anions) for use in the treatment of water contamination.

ACGO beads provide higher tensile strength than AC beads because ACGO beads contain graphene oxide that acts as a reinforcing filler. Graphene oxide (GO) has higher aspect ratios than many nano size fillers. Its better mechanical properties than many polymers. So, they are preferred as filler material in composite material [29]. Moreover, the graphene oxide consists of hydroxyl, carbonyl, and carboxylic

acids functional groups that can cause strong hydrogen bonding with amorphous cellulose, resulting in the tensile strength of ACGO higher than AC.

There are various techniques to measure nitrite level in water. Those techniques consist of spectrophotometric methods, chemiluminescent, electrochemical detection, chromatographic, capillary electrophoresis, spectrofluorimetric and electro chemiluminescent methods [30].

1) Spectrophotometric methods

1.1 Griess assay

The spectrophotometric detection of nitrite is the Griess Assay which involves a diazo-coupling procedure. The main principle of this method is that under acidic conditions, nitrite reacts with sulfanilic acid to form a diazonium cation which subsequently couples to the aromatic amine 1-naphthylamine to produce a red-violet coloured (λ_{max}≈540 nm), water-soluble azo dye. However, the reagent 1-naphthylamine used in this method is carcinogenic.

1.2 Nitrosation-based spectrophotometric methods

Nitrosation reaction is also applied to the determination of nitrite. Several other indicating species react with nitrite to give coloured products. For example, nitrite reacts with barbituric acid in acidic solution to give violuric acid, a nitroso derivative. Based on it, a spectrophotometric method for the determination of nitrite in water has been developed. At analytical wavelength of 310 nm, Beer's law is obeyed over the concentration range 0.00 – 3.22 ppm of nitrite. Moreover, a novel spectrophotometric reaction system for the determination of nitrite as well as nitrate in water samples based on the nitrosation reaction between nitrite ion and phloroglucinol (1,3,5-trihydroxybenzene). The system was applied to a flow-injection analysis and up to 20 samples can be analyzed per hour with a relative standard deviation of less than 1.5%. However, the absorbance maximum of the product is at 312 nm, making the procedure is significantly influenced by Fe^{3+}.

1.3 Catalytic-spectrophotometric methods

Catalytic-spectrophotometric methods are mainly based on the catalytic effect of nitrite on the oxidation of some indicating species or organic dyes with suitable oxidizing agents. These methods for determination of nitrite require strict control of reaction conditions such as acidity, temperature and reagent dosage.

To make further development to these methods, the following efforts should be made: (1) make use of surfactant in some indicating reactions to improve sensitivity and selectivity; (2) pay more attention to illustrating the mechanism of the catalytic action, thus finding an effective way to improve sensitivity and selectivity; (3) develop novel highly sensitive and specific indicating agents, improve their water-solubility; (4) apply FIA system to catalytic-spectrophotometric methods to improve the efficiency of analysis.

2) Chemiluminescent

Chemiluminescence (CL) is known as a powerful analytical technique that possesses numerous advantages such as simplicity, wide linear range, low cost, safety and controllable emission rate.

3) Electrochemical detection

Electrochemical techniques based on various modified electrodes are favored owing to their inherent simplicity, high sensitivity and selectivity. Modified electrodes with suitable catalyst not only improve reduction response of nitrite, but also extend the dynamic range in analytical determinations. A variety of modified electrodes used for nitrite determination are metal and metal oxide nanoparticles and nanoclusters, carbon nanotubes (CNTs), Chitosan (CS), organic and inorganic electropolymerized films.

4) Chromatographic

Direct sample analysis can be achieved by most HPLC and ion chromatography techniques.

4.1 HPLC

The detection principles of HPLC analysis include UV and VIS absorbance, electrochemistry, chemiluminescence, and fluorescence (Table 4). Nitrite and nitrate can be directly measured by UV absorbance detection at 210–220 nm or by their conductivity.

4.2 Ion chromatography

Using the solid phase extraction method (SPE) and next for its quantitative determination by applying the ion chromatography technique with conductometric detection [31].

5) Capillary electrophoresis

Capillary electrophoresis (CE) is a versatile technique which can be used to analyze cationic, anionic and neutral compounds.

6) Spectrofluorimetric

Spectrofluorimetric methods are based on the changes of fluorescence intensity when fluorescent probes reacted with nitrite. Many fluorescent probes for the determination of nitrite have been developed by utilizing the chemical specificity of nitrite ion to undergo nitridation/diazotization.

7) Electrochemiluminescent methods

Electrochemiluminescent (ECL) detection of nitrite based on its quenching effect on anodic ECL emission of CdSe quantumdots (QDs). The nitrite quenched ECL emission could be analyzed according to the treatment of Stern-Volmer equation, and a linear range from 1 μM to 0.5 mM for detection of nitrite was given.

Activated carbon is currently less expensive than graphene oxide and TEMPO-oxidized CNFs, but nearly as expensive as microcrystalline cellulose. Table 2.2 compares the adsorption capacities of microcrystalline cellulose and activated carbon. Furthermore, TEMPO-oxidized CNFs are produced using an expensive synthesis method; alternative methods may yield cheaper CNFs. Because of their higher adsorption capacity, CNFs and graphene oxide are promising candidates for replacing activated carbon materials.

Table 2.3 Raw material price [32]

Material	Price per kilogram (US $)
Tempo-oxidized cellulose nanofibers (CNFs)	4.0-6.0
Microcrystalline cellulose	2.5
Graphene oxide (GO)	100.0-170.0
Reduced graphene oxide (RGO)	55.0-69.0
Activated carbon (AC)	1.0-3.0
Carbon nanotubes (CNTs)	20.0-100.0
Chitosan	20.0-50.0

2.3 Market analysis

The market analysis focuses primarily on the water remediation market, which is divided into the following water contaminant types: drinking water contaminants, antibiotics, and contaminants in industrial wastewater treatment systems. Therefore. The ACGHOS has the potential to be commercialized in three adsorption markets: household drinking water cartridge market, hospital water treatment system adsorbent material, and industrial water treatment system adsorbent material. Each market has different adsorption efficiency requirements, particularly drinking water, which requires high efficiency adsorbent to adsorb small particles such as NPs, MPs, and heavy metals, making ACGOHS one of the best alternative materials for drinking water adsorbent.

2.3.1 Household drinking water cartridge market

The ACGOHS could be used as a new material in cartridges or in combination with other filtering materials. A growing trend for a healthier option is fueling the growth of the drinking water and water remediation markets. The healthy trend and pure water consumption rate have been increasing, with the pure water consumption rate increasing by 12.97% from 2018 to 2019 (approximately 45,300 million baht market value for bottle water market) [33].

The majority of bottled water market revenue is generated in the United States, with a volume of 61,076 million US dollars in 2020. The top four bottled water market volumes were the United States (US$ 61,076 million), China (US$ 53,337 million), Mexico (US$ 15,422 million), and Germany (US$ 14,524 million). In 2020, Thailand's market volume was 1,606 million US dollars, or approximately 49,786 million Baht. Thailand's water purifier market value was approximately THB 12,000 million. Thiensurat PLC. (TSR), Amway, and Coway are the major players in Thailand's water purifier market [34]. TSR generated revenue of about 1,636 million baht in 2019 calculated as 14% market share, Amway generated revenue of about 2,300 million baht in 2019 calculated as 38% market share, and Coway generated revenue of about 1,000 million baht in 2019 calculated as 8% market share [34].

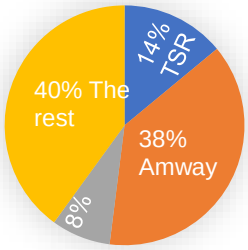


Figure 2.1 Thailand water purifier market share [34]

The researcher chose three popular Thiensurat product series for cartridge analyzing: mineral plus, RO Plus+, and i-life. The E-Spring (Amway water purifier) only has one cartridge, which is activated carbon [35]. Components of both the TSR and Amway water purifiers are shown in Table 2.4.

Table 2.4 Cartridge materials and commercial price [34, 35]

Brand	Filter	Water Purifier (Baht)	Cartridge (Baht)	Life time
RO mineral plus	1. Ceramic pre-filter 2. Sediment cartridge 3. Activated carbon I 4. Activated carbon II 5. RO membrane 6. Silver impregnated mineral stone 7. Post carbon	16,900	4,900	2 years or 20,000 L
RO Plus+	1. Pre-filter 2. Activated carbon I 3. Activated carbon II 4. RO membrane 5. Alkaline mineral stone 6. Post carbon	16,900	4,900	2 years or 20,000 L
i-life	1. Pre-filter 10 micron 2. Activated carbon + KDF55 + SIAC I 3. UF membrane + SIAC II	5,500	1,700	1 year or 20,000 L
E-spring	Activated carbon	29,970	4,840	1 year or 5,000 L

2.3.2 Adsorbent market for hospital wastewater treatment system

Antibiotics are commonly detected in hospital and pharmaceutical factory water effluent due to antibiotic residues contaminating the wastewater treatment system. In 2016, there were 347 private hospitals divided into four categories based on the number of beds: A (less than 31 beds), B (31-50 beds), C (51-100 beds), and D (more than 100 beds). For types A, B, C, and D, there were 83, 46, 100, and 118 hospitals, respectively. In addition, there were 294 public hospitals with more than 100 beds in 2019 [36].

Wastewater treatment in hospital consists of a wastewater collection system, equalization tank, aeration tank (secondary treatment), sedimentation tank, activated sludge system, chlorine tank and effluent system. The wastewater system capacity for hospital classes A, B, C, and D is 1 m^3/bed per day [37]. Therefore, total wastewater system capacity in both Thailand private and public hospital is minimum 23,713 m^3/bed per day.

Table 2.5 Thai hospital wastewater capacity [37]

Type	No. of bed	No. of hospital	Wastewater capacity (m^3/day)
A	31	83	2,573
B	31-50	46	1,840
C	51-100	100	7,500
D	>100	118	11,800

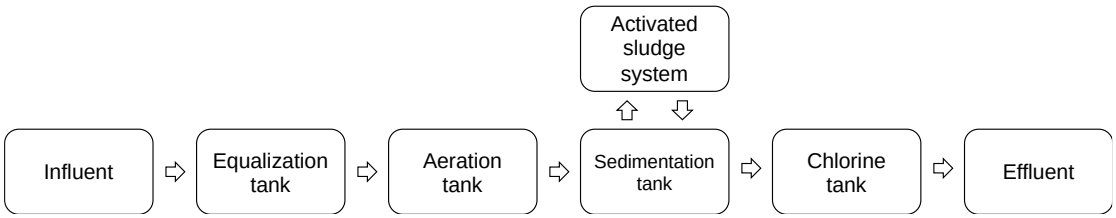


Figure 2.2 Siriraj hospital wastewater treatment system [37]

As shown in Figure 2.3, the ACGOHS could be an additional applicable adsorbent for adsorbing antibiotics instead of activated carbon adsorption. The market value of the ACGOHS in Thai hospital wastewater treatment systems will be calculated in the commercialization chapter.

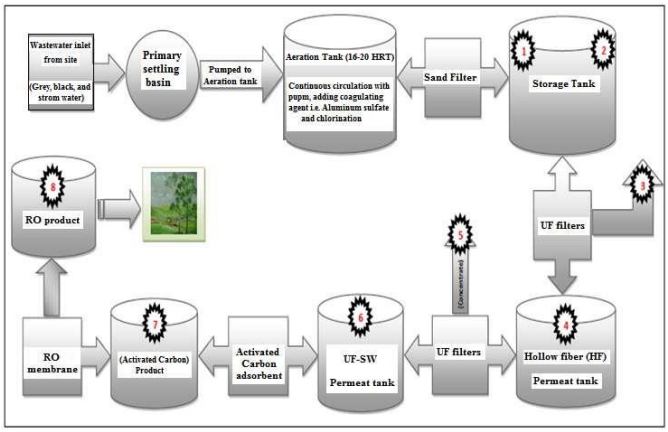


Figure 2.3 The process of wastewater treatment plant [4]

There are various types of antibiotics used in hospitals as shown in Table 2.6.

Table 2.6 Classification of antibiotics [38]

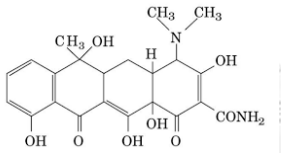
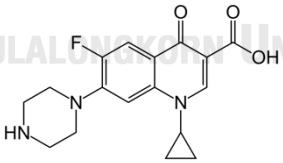
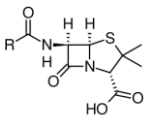
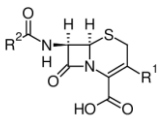
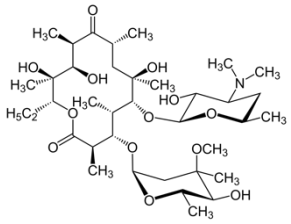
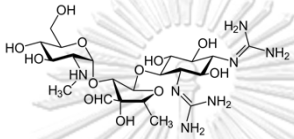
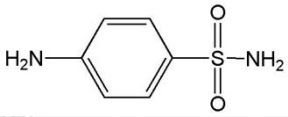
Antibiotic type	Material structure	Representative	Abb.
Tetracyclines		Tetracycline	TCN
		Doxycycline	CTC
		Chlortetracycline	OTC
		Oxytetracycline	TC
Quinolones		Ciprofloxacin	CIP
		Norfloxacin	NFC
		Oqidos	
		Ofloxacin	OFC
β-lactams	 Penicillins  Cephalosporins	Pennicillin	PN
		Amoxicillin	AXC
		Cephalosporins	
		Monobactams	
		Carbapenem	

Table 2.6 Classification of antibiotics (continued) [38]

Antibiotic type	Material structure	Representative	Abb.
Macrolides		Tylosin Roxithromycin Eryphilin Avermercin	REM
Aminoglycosides		Streptomycin Ampicillin Gentamicin Kanamycin Tobramycin	
Sulfonamides		Sulfazazole Sulfadiazine Sulfamethoxazole	 SD SMT

The top antibiotic prescribed at Mahasarakham hospital were ceftriaxone (CEF), cefazolin (CZ), ceftazidime, ampicillin, amoxicillin (AMOX), clavulanate and ciprofloxacin (CIP) [39]. In Songkhla, the four most common antibiotic prescriptions were ceftriaxone (CEF), ciprofloxacin (CIP), norfloxacin (NOR), and tetracycline (TC). Three hospital wastewater treatment plants in Songkhla achieved removal efficiencies of up to 100% (CEF), 70.5% (CIP), 63.5% (NOR), and 98.3% (TC). Furthermore, dicloxacillin (DX), piperacillin (PC), cefalexin (CFX), cefazolin sodium (CZ), clarithromycin (CM), ciprofloxacin (CIP), metronidazole (MD), and sulfamethoxazole (SMX) were the most commonly prescribed antibiotics in Thai hospitals [40].

2.3.3 Adsorbent market for industrial wastewater treatment system

The majority of research focuses on heavy metals and dyes for water contaminants in industrial wastewater treatment systems, as shown in Table 2.2, but VOC contaminants must also be considered.

VOCs are commonly detected in industrial sections, both in the air and wastewater systems. VOCs are becoming public pollutants as a result of Thai transportation and construction projects, not just in the industrial sector. In 2019, it was recorded that there were 16,283 factories located within Bangkok and 122,524 factories located outside of Bangkok [41].

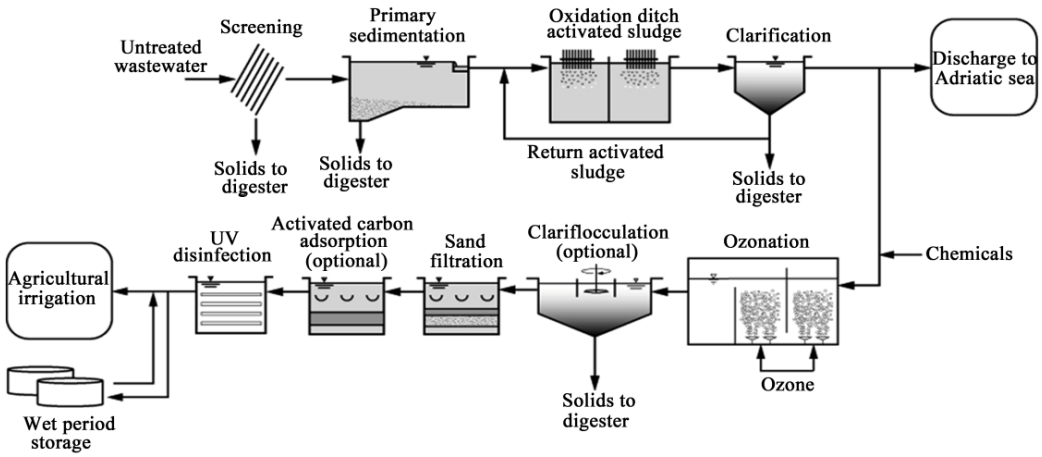


Figure 2.4 Process flow diagram for the Foggia factory wastewater treatment system [42]

The ability of graphene-based adsorbents to adsorb VOCs such as aromatic, aliphatic, alcoholic, and chlorinated VOCs was demonstrated [7]. As a result, the ACGOHS could be used as adsorbents in industrial water treatment systems instead of AC.

2.4 Product validation

The ACGOHS characterization study and the ACGOHS adsorption capacity study will be divided into two main topics for product validation. The morphology of the ACGOHS will be visualized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) micrographs. The ACGOHS functional

groups will be presented using Fourier transform infrared spectroscopy (FTIR). The Raman spectra (Raman) will be used to demonstrate the ACGOHS defect, and the Brunauer-Emmett-Teller (BET) will be used to demonstrate the ACGOHS surface area. The same set of tools will be used to characterize the ACGOHS after the adsorption process is completed [43]. The adsorption kinetic and isotherm models, as well as density functional theory (DFT), will be used to investigate the adsorption mechanism [7, 8, 27]. In depth detail will be explained in the latter chapter.

2.5 Cellulose

Wood is the most commercialized cellulose resource. Eucalyptus is a woody plant that is very attractive as a raw material because it contains less hemicellulose, lignin, and additives than other woody plants such as rubber wood [24].

The researcher has collected reviews of chemical composition of raw cellulosic materials from different sources as shown in Table 2.5.

Table 2.7 Chemical composition of raw cellulosic material [44]

Material	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Extractives (%)
Rubberwood				
Unbleached fibers	45.0±3.0	20.0±2.0	29.0±2.0	2.5±0.5
Bleached pulp	91.0±1.0	5.0±1.0	4.0±1.0	0.5±0.1
Nanofibers	92.0±1.0	4.0±1.0	3.0±1.0	0.5±0.1
Eucalyptus				
Raw	85.3	13.9	0.1	0.1; ash = 0.6
Soy hulls				
Initially (raw)	48.2 ± 2.1	24.0 ± 3.0	5.78±1.1	-
Treated (purified)	84.6±4.0	11.2±4.0	3.7±0.3	-

The cellulose content of eucalyptus kraft pulp (raw) is 85.3 percent, which is higher than that of other woods. Rubberwood contains only 45 ± 3 percent cellulose when unbleached and 91 ± 1 percent when bleached. However, the bleaching process is more expensive and energy-intensive, so synthesizing cellulose from bleached eucalyptus kraft pulp is preferred due to its low cost and ease of operation.

2.5.1 Cellulose structure

Cellulose has a supramolecular structure with an intramolecular and intermolecular hydrogen bond network that connects one glucose unit to its neighbors in both the same and neighbor chains. For chain stiffness and two-fold crystalline cellulose conformation, intramolecular interaction occurred between O3-H and O-5' of adjacent units and O2-H and O-6' with neighboring glucose units. Intermolecular hydrogen bonds form between neighboring chains' O-6-H and O-3 for interchain cohesion and packing [45].

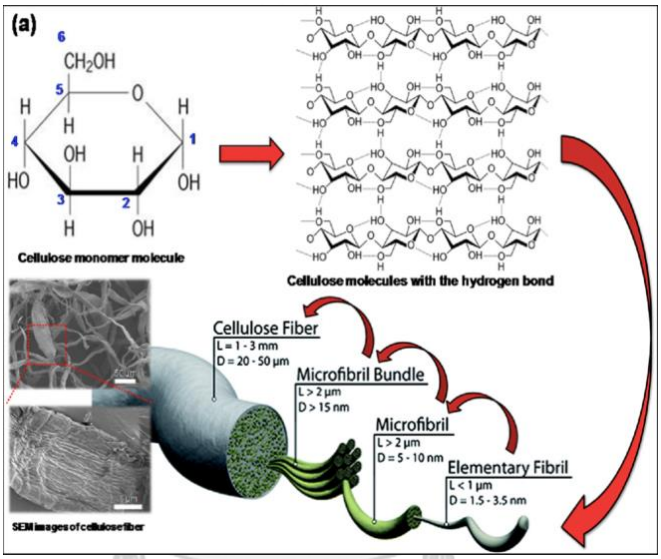


Figure 2.5 Cellulose fiber formation and its structure [46]

Numerous cellulose chains composed into protofibrils, then packed into microfibrils, finally they become cellulose fiber by having Van De Waals and inter-intramolecular hydrogen bonding [47]. There are various types of cellulose such as nanocrystalline cellulose (NCC), cellulose acetate, bacterial cellulose (BC) and regenerated cellulose (RC) [46].

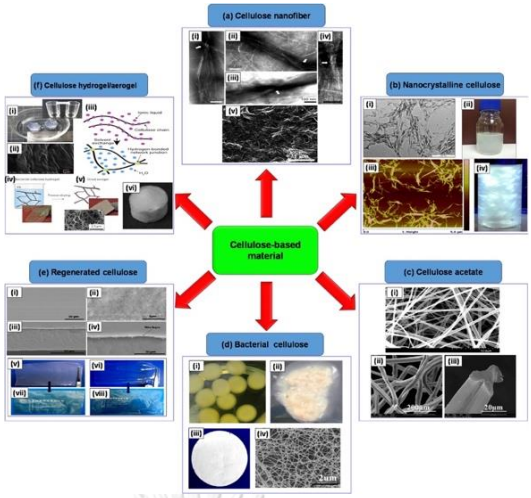


Figure 2.6 Different types of cellulose [46]

Because of its molecular structure, cellulose has the strength, stiffness, and flexibility to be used in environmental products. From 2014 to 2016, the market demand for nanocellulose increased by 33.8%, from US$ 54.19 million to US$ 87.5 million. Publications and patents confirm the trend of nanocellulose. Cellulose is used in three major industries: food, water, and energy [1]. Table 2.8 summarizes nanocellulose applications, which are divided into three categories: high volume applications, low volume applications, and novel and emerging applications.

Table 2.8 Application of nanocellulose [45]

High volume applications	Low volume applications	Novel and emerging applications
Cement	Wallboard facing	Sensors-medical, environment, industrial
Automotive body	Insulation	Reinforcement fiber construction
Automotive interior	Aerospace structure	Water filtration
Packaging coatings	Aerospace interiors	Air filtration
Paper coatings	Aerogels for the oil and gas industry	Viscosity modifiers
Paper filter	Paint-architectural	Purification
Packaging filler	Pain-special purpose	Cosmetics
Replacement-plastic packaging	Paint-OEM applications	Excipients
Plastic film replacement	-	Organic LED

The two regions in the cellulose microfibril structure are crystalline and amorphous regions, as Figure 2.7 [45]. Since amorphous region is disordered, it has lower density but higher volume than crystalline region.

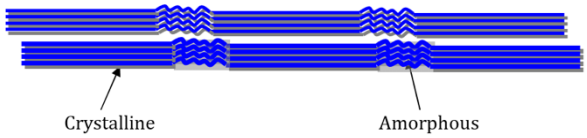


Figure 2.7 Crystalline and amorphous regions in cellulose microfibril [45]

2.5.2 CNCs and CNFs cellulose extraction

Nanocellulose can be produced in four steps. To begin, pretreatment was used to remove dust, oily content, and contaminants from the surface of the material. Second, chemical, mechanical, or enzymatic methods were used to remove the inner cellulose fibrous content, which includes glycoprotein, pectin, hemicellulose (in the plant primary cell wall) and lignin and hemicellulose (macrofibrils) in the plant secondary cell wall. The third step is to fragment the CNFs or CNCs using hydrolysis or mechanical destruction. The final step is surface modification to achieve the desired function [1].

Table 2.9 Nanocellulose synthesis process [1]

Step	Process
1	Pretreatment
2	Inner cellulose fibrous content elimination
3	Fragmentation
4	Surface modification

Nanocellulose is divided into two types, cellulose nanofibrils (CNFs) and cellulose nanocrystals (CNC) [10]. Cellulose microfibril (MFC) is easier to prepare and has a higher yield. Furthermore, it can be used in a variety of applications such as thickeners, emulsifiers, and additives in food, paints, and coatings. Unlike CNC, amorphous cellulose has a high yield because the amorphous region is not extracted during the extraction process [48]. There were many CNFs in the plant cell wall,

which is the main component in plants, providing strength and stiffness. CNFs are cellulose polymers with lengths of a few microns and an amorphous and crystalline region [49]. By removing the amorphous region that is sensitive to hydrolysis, a crystalline region can be obtained. Because the properties of CNC and CNFs differ, they are used in different applications.

2.6 Graphene oxide

Because of its hydrophobicity, graphene cannot be combined with nanocellulose in the water treatment process. However, graphene can be used to reduce the viscosity of crude oil, which has a viscosity of 100-10,000 mPa at room temperature. Because graphene has a high hydrophobicity, it is difficult to use for water remediation. As a result, a material with similar functions to graphene is required to replace graphene in order for it to be combined with cellulose in an aqueous environment. Graphene oxide (GO) and reduced graphene oxide (RGO) are two materials that are similar to graphene [50].

Graphene oxide is a graphene material that has been modified. It is composed of many oxygens with numerous functional groups at the edges such as epoxides, hydroxyls, and carboxyls [51]. Not only are some properties of graphene unsuitable for inclusion in water treatment products, but the cost of producing graphene is also an issue. One of the most interesting materials directly related to graphene is GO because it is cheap and abundant in the market [52]. GO has a large surface area (around 2,630 m2/g), is mechanically flexible, has a high mobility of charge carriers, and is chemically stable [24]. Four different methods, including Staudenmaier, Hofmann, Brodie, and Hummers, are being used to create graphene oxide [52]. The Brodie and Staudenmaier methods take into account the explosion risk and provide hazardous gases production. Due to Mn_2O_7, the Hummer process has a high danger of explosion, requires extensive oxidation, and is expensive [53]. Furthermore, four synthesis strategies of graphene-based hybrids and composites were used, including dip-coating, surface coating by inti generation of graphene via thermal treatment, in its incorporation process, and hydrothermal process in the presence of gelation-causing agent [54]. Lastly, the methodologies for synthesis of three-dimensional

graphene-based hybrid materials for water purification include template-based synthesis, self-assembly, freeze-drying, and 3D printing [1].

Table 2.10 Graphene-based material price [32]

Type	Characteristic	Price ($/kg)
Graphene		6.40-7.00
Graphene Oxide		0.98
Reduced graphene oxide		1,490
Activated carbon		0.95-1.25

2.7 Composite material

The combination of graphene oxide and cellulose improves the properties of either material alone. When a layer of graphene oxide was used as a composite material with CNFs, the pore size was reduced and the water flux increased. Furthermore, it removed more than 90% of the dyes [55].

2.7.1 Existing technology to produce the ACGOHS

Cellulose-graphene oxide composites are produced by numerous methods. Each method uses different raw materials and techniques collected as summarized below.

Table 2.11 Existing technology to produce nanocellulose/graphene oxide hybrid products

Product	Product Form	Raw material	Technique
Cellulose/graphene oxide fibres [56]	Fibre	Graphite, sodium cellulose xanghate (8.35 wt %)	Wet spinning
Self-assembled TEMPO cellulose nanofibers: graphene oxide-based biohybrids [57]	Suspension and films	TOCNF, nanoGO	Vacuum filtration
Hybrid monolith of graphene/TEMPO-oxidized cellulose nanofiber [24]	Monolith	Graphite, CNFs	Urea assisted self-assembly method
Nanocellulose-graphene oxide hybrid aerogel [25]	Aerogel	Amorpha fruticosa, Graphite	A freeze-drying process
Nanocellulose/graphene oxide layered membranes [55]	Layered membranes	CNFs (1.8 %wt), GO suspension	Vacuum filtration
Cellulose nanofibril/graphene oxide hybrid aerogel [27]	Aerogel	CNFs, GO	One-step ultrasonication
CNC/graphene hybrids [58]	CNC-GO	Film	Blending method

2.8 Scaling up process

To commercialize the product, it must be manufactured in large quantities in order to complement the scaling up process. The scale-up framework is comprised of five steps: a laboratory protocol, a plant flow chart with scale and reactor sizes, the separation of each process step, the linking of process steps, and the performance of a life cycle assessment (LCA).

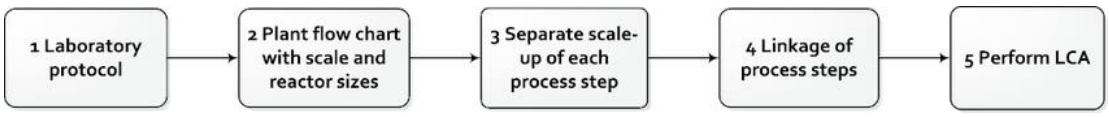


Figure 2.8 Overview of scale-up procedure [10]

In the scale-up process, four key factors must be concentrated: input value (reaction step), input value (processing, purification, and isolation steps), output value, and infrastructure, which will be discussed in detail in the following chapter [10].

2.9 New product development process

The goal of this project is to develop a product using new methodology or technology. It is, on the other hand, incremental product development. Breakthrough or radical product development and incremental product development are the two types of new product development. Because of the reasons summarized in Table 2.8, this project is an incremental development product.

Table 2.12 New product development process [59]

Breakthrough/radical product development	**Incremental product development**
1. New technology	1. Existing technology
2. Long time development	2. Changing follows customer need and technology
3. High technology	3. Effort to entry market
4. High risk in marketing	4. Market development
5. New solution/ new benefits/ new value	5. Create new look and feel
6. Newness to the World	6. Decrease cost
7. Expand to unmet need/unconscious customer group	7. Development in production or existing manufacturing line
-	8. Improvement in existing business line
-	9. Sustain existing customer base

The ACGOHS is an incremental product because the main component material of the ACGOHS is already on the market, but the processes used to produce the

ACGOHS are novel. Table 2.13 shows the researcher's proposed new product development process (NPD) for the ACGOHS.

Table 2.13 New product development process (NPD)

Boer (1999)	**Cooper (2001)**	**Schroeder (2003)**	**Ulrich and Eppinger (2004)**	**Alexandra (2009)**	**Proposed NPD**
5 stages	6 stage-gate system	3 stages	5 stages	5 stages	4 Stages
Raw ideas	Discovery	Concept development	Concept development	Product concept	Product feasibility
Conceptual project	Scoping	Product design	System level design	Feasibility	Product production and validation
Feasibility	Business case	Pilot production/ testing	Detail design	Development	Mass scale production
Development	Development	-	Testing and refinement	Validation	Commercialization
Early commercialization	Testing and validation	-	Production ramp-up	Commercialization	
-	Launch	-	-	-	

There are four stages in the new product development process to implement incremental product development: product feasibility, production and validation, mass scale production plan, and commercialization.

Details of each stage to implement the ACGOHS filter are described as follows.

1) Product feasibility

Product feasibility includes market analysis, product design, finance, and opportunities. Because activated carbon, the main existing material for water treatment, has long-term effects on the environment, ecosystems, and human health, an alternative environmental material must be developed to replace activated carbon. An alternative material must be at least as good as the existing material and environmentally friendly. The ACGOHS has biocompatibility, biodegradability, and renewable properties. Indeed, the overall adsorption capacity of heavy metals and other contaminants is greater than that of activated carbon. Because the new raw material has better properties for drinking water treatment than activated carbon,

replacing activated carbon with ACGOHS is a great opportunity to introduce new environmentally friendly materials to the water remediation industry. The product standard will be established after market benchmarking. Quality control, quality assurance, and safety protocols in manufacturing, as well as efficiency measurement, will be implemented to ensure product safety and consistency.

2) Product production and validation

Following the completion of stage one, the product implementation will begin. The ACGOHS will be implemented in the laboratory before being scaled up to a larger and near commercialization scale. The purpose of validation is to test the product's efficiency and characterization. The specifics will be covered in the following chapter.

The mass scale production plan will be implemented to answer objective 3. Details of the mass scale production plan will be described in the latter chapter.

3) Commercialization

To answer objective 4, the commercialization plan will be implemented in accordance with the business plan and business theory. The details will be described in the following chapter.

Chapter 3
Research methodology

In the previous chapter, literature review on water contaminants, existing technology for water remediation, antibiotics, volatile organic compound (VOCs), pesticides and opportunity in potential markets were examined. The research methodology will be implemented in this chapter. According to the objectives, the research process is divided into four stages, which are summarized in Table 3.1.

Table 3.1 Research methodology

Phase	Objective	Method	Outcome
1. Study existing ACGO bead manufacturing, IP surveys, and production designs	To study and develop innovative process to produce the ACGO bead	Qualitative approach	Innovative methodology of ACGO bead fabrication
2. Develop the ACGO bead prototype and validate the product	To develop the ACGO bead prototype through new innovative process and validate the product	Experiment design and quantitative approach	ACGO bead and characterization
3. Develop mass scale production process	To apply the design of experiments (DOEs) for mass scale production process	Qualitative approach	A scaling-up production plan
4. Implement commercialization plan	To commercialize and launching plan	Qualitative and quantitative approach	Commercialization plan

The research is divided into four phases as following:

Phase 1: This phase includes an examination of existing ACGO manufacturing, IP surveys, and production designs. The ACGO innovative manufacturing process will be implemented as a result of this phase.

Phase 2: This phase is divided into two stages: developing the ACGO bead and validating it. The ACGO bead prototype will be obtained as a result of this phase, and its validation will include a study of its morphology and adsorption capacity.

Phase 3: This phase involves putting the large-scale production plan into action in order to simulate the lab-scale to near-commercialization scale plan.

Phase 4: This phase involves putting the commercialization plan into action in order to study the ACGO bead market and the possibility of launching the product.

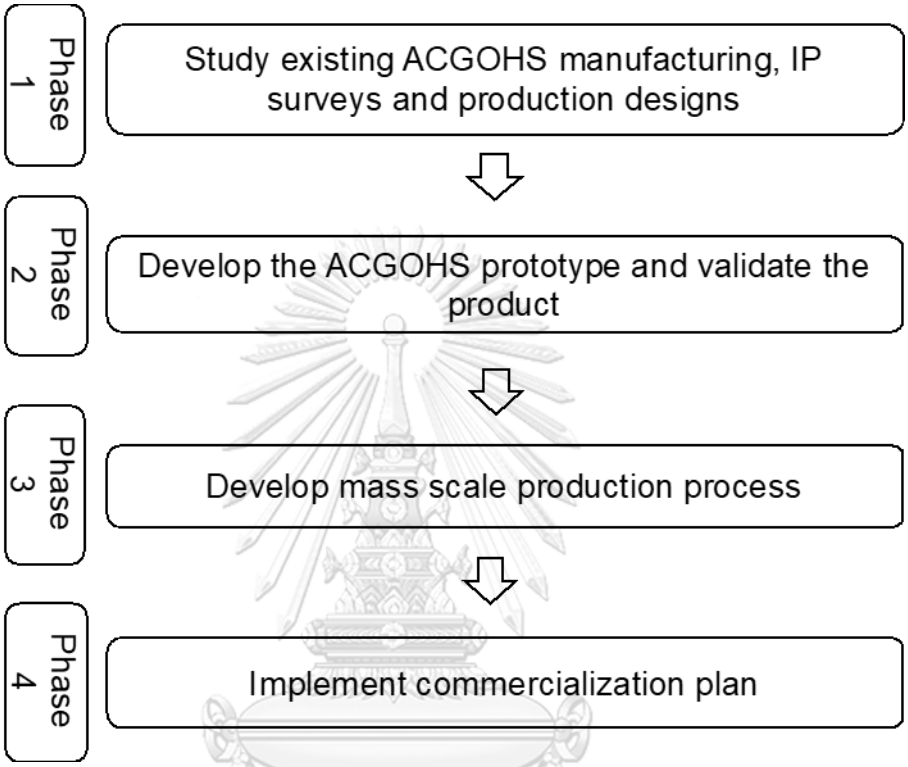


Figure 3.1 Research methodology diagram

3.1 Phase 1: Study existing ACGO bead manufacturing, IP surveys, and production designs

3.1.1 Raw material

There are two reasons why bleached eucalyptus was chosen as a raw material. For starters, it has a high cellulose content. Second, it is the Thai economic tree, so using bleached eucalyptus as a raw material may drive the eucalyptus market. Furthermore, the researcher decided to begin the amorphous cellulose extraction process with bleached eucalyptus rather than raw eucalyptus because the cost of bleached eucalyptus is less than the cost of starting the bleaching process. Pre-treatment, chemical hydrolysis, and separation/purification were the three chemical processes used to obtain nanocellulose [1].

3.1.2 Solvent and anti-solvent

Sulfuric acid was chosen as the solvent, and water as the anti-solvent. Organic solvents, ionic liquids, and NaOH medias such as ionic liquid solution of 1-allyl-3-methylimidazolium chloride, LiCl/DMAC system, 6%wt NaOH/4%wt Urea solution, sulfuric and phosphoric acid were all used to dissolve cellulose. According to Kazuyuki (2016), the disadvantages of phosphoric acid, ionic liquids, NaOH or NaOH/urea aqueous solution, NMMO/H_2O, and LiCl/N,N-dimethylacetamide (DMAc) are the high dissolution temperature, difficulty in solvent recovery, and high cost [60].

Table 3.2 Price of various solvent types [32]

Solvent	Market price ($/kg)
Carbon disulfide (CS_2)	10 - 25
Lithium chloride/N, N-dimethylacetamide (LiCl/DMAC)	1 - 2 (LiCl) 5 - 18 (DMAC)
N-methylmorpholine-N-oxide (NMMO)/water	3.5 - 6.0 (NMMO)
Ionic liquid	12.90 - 14.30
NaOH/urea aqueous solution	0.5 - 0.9 (NaOH), 0.6 - 2.5 (Urea)
Phosphoric acid	0.6 - 1.0
Sulfuric acid	0.5 - 1.0

However, the use of phosphoric to dissolve cellulose resulted in a low dissolution efficiency. Previous research used 64% sulfuric acid to create cellulose nanocrystals. The solvent 70% w/w sulfuric at 5C was chosen because it provides 97.6% yield [61]. In the regenerated process, water is chosen as an anti-solvent. Water and ethanol are common anti-solvents used in the regenerated process for precipitating cellulose. Water as an anti-solvent produced more crystallinity than ethanol (43.33 - 21.27%) [62]. Furthermore, water is inexpensive and abundant in comparison to ethanol, which costs 1-2 US dollars per kilogram [32].

3.1.3 Existing methodologies to produce cellulose products and cellulose-GO composites.

Methodologies to produce cellulose and cellulose-GO composites were collected and summarized in Table 3.3 and the new methodology was proposed to produce the ACGOHS.

Table 3.3 Existing cellulose and cellulose-GO production methodologies

Product	Dissolved and regenerated methodology
Ag@HPAMAM NPs-embedded cellulose film [63]	Cotton fiber is used as raw material. NaOH/urea solution and $NaIO_4$ is used for cellulose dissolution. Ag@HPAMAM NPs solution is added to the oxidized cellulose solution. Ethanol is used as an anti-solvent and the film obtained by nature drying.
Amorphous cellulose thin films [64]	Microcrystalline cellulose (Avicel PH101, MC) is used as raw material. Mixtures of ionic liquids and organic solvents (1-ethyl-3-methylimidazolium acetate (EMIMAc) and dimethyl sulfoxide (DMSO)) is used for dissolution solvent. Acetone or ethanol is used ant-solvent.
Regenerated cellulose Hydrogel [62]	Microcrystalline cellulose (PH101, MCC) is used as raw material. 1-ethyl-3-methylimidazolium acetate ionic liquid [Emim][OAc] is used as dissolution solvent. Anhydrous ethanol or water is used as anti-solvent.
Regenerated spruce cellulose film [47]	2 g of spruce cellulose is mixed with 64 %wt (pre-cooled to – 20 °c) rotated at speed 800 rpm for 5 mins, then centrifuged for 5 mins, subsequently mechanic stir for 10 mins at 0-4 °c via 10 %w/v NaOH aqueous solution as anti-solvent.
Regenerated cellulose [65]	0.2-0.6 g MCC powder with 0.6 mL DI water is added to a 50 mL centrifuge tube. 10 mL precooled 85 wt % H3PO4 is added and mixed by a vortex. The homogenous solution is regenerated by water. The yield of regenerated cellulose is 86.6 % while the optimum yield of CNCs is 30%. The scale-up ratio of cellulose/water/85 wt % H3PO4 is 1:3:50 (w/v/v) at 5 °c and 24 h.

Table 3.3 Existing cellulose and cellulose-GO production methodologies (continued)

Product	Dissolved and regenerated methodology
Amorphous cellulose hydrogel [61]	MCC power mixed with 70% w/w H_2SO_4 (1 g cellulose/10 mL H_2SO_4), using ethanol (-17 °c) or water (4 °c) as anti-solvent with equivalent acid usage amount. The result shown that 97% yield of regenerated cellulose obtained via constraint of 70% acid concentration, 5°c treatment temperature, 30 mins stirring time via using ethanol as anti-solvent, while obtaining 72.7 % yield if use water as anti- solvent (other parameters are the same).
Regenerated cellulose Microspheres (RCM) [66]	Cotton linter pulp is used as raw material, NaOH/urea/H_2O is used as solvent and Paraffin oil is used as anti-solvent.
CNCs-GO composite [43]	GO obtained by the Hummer method was mixed with the CNCs suspension, subsequently freeze-dried to obtain the CNCs-GO hydrogel.
Graphene oxide/cellulose nanofibril hybrid aerogel [27, 67]	80 mg cellulose and 100 mg GO are put in 100 mL DI water under vigorous ultrasonication for 30 min in ice bath. The solution was frozen at -30 °c for more than 5 h. Subsequently, the solution was freeze-dried at -55 °c for 48 hours.
CNC-alginate hydrogel bead [68]	Mixed 0.2-2 %wt CNCs and 1-4 %wt sodium alginate solution in a homogenizer. The bead sized controlled by 22-gauge size needles by using 50 mL of 2 %wt $CaCl_2$ as anti-solvent with condition of 5 mL/min flow rate
The proposed ACGOHS bead methodology	Bleach eucalyptus is chosen to be raw material because of lower cost than starting at bleaching process and 70% w/w H_2SO_4 @0°c is chosen to be cellulose solvent because the previous presented that at 5°c, 70% w/w H_2SO_4, proportion of raw material to solvent amount (1g:10 mL), 30 mins stirring time and ethanol as anti-solvent gave 97.4 % yield generated cellulose. GO will be mixed with cellulose-sulfuric solution when the cellulose suspension color is transparent because in this phase H_2SO_4 breaks H-bonding occurring gap for GO to be embedded. The ACGOHS solution will be loaded to the syringe pump and extrude to be the ACGOHS bead by using water as anti-solvent.

The ACGOHS bead protocol is implemented in Table 3.3 and the experiment was implemented in topic 3.2 to prove that the proposed protocol could produce the low cost and highly efficient ACGOHS bead.

3.2 Phase 2: Develop the ACGO bead prototype and validate the product

The objective of this phase is to develop the ACGOHS prototype using a new innovative process and to validate the product. This phase is divided into two separate stages: ACGOHS bead implementation and validation.

3.2.1 Experiment of AC and ACGO bead fabrication

The researcher implemented the ACGOHS bead production methodology flow as shown Figure 3.2.

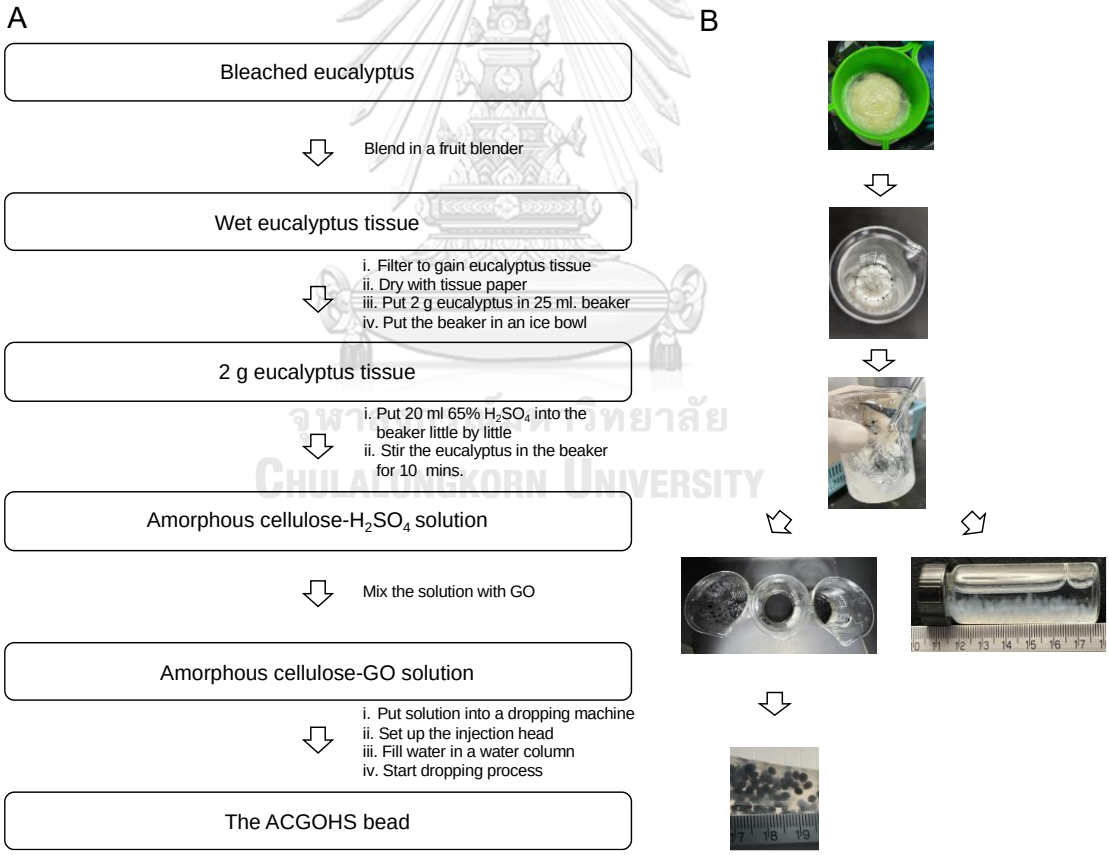


Figure 3.2 Schematic diagram showing (A) the ACGOHS production process (B) the ACGOHS and amorphous bead phototype

The synthesis of amorphous cellulose began with pulverizing bleached eucalyptus in a fruit blender. The wet eucalyptus and tissue were filtered and dried with tissue paper to remove the water and obtain only wet eucalyptus tissue, then 2 g eucalyptus was placed in a 25-mL beaker in an ice bath. The eucalyptus tissue in the beaker was gradually added with 20-mL 70% sulfuric acid (H_2SO_4) into the beaker and while being stirred for 10 minutes, until the solution became transparent and viscous. When scaling up production, the ACGOHS-H_2SO_4 solution should be prepared in large quantities by collecting it in a large beaker and storing it in a refrigerator at 0 ℃. Keeping the amorphous cellulose-H_2SO_4 solution in the refrigerator aimed to keep the swelling reaction going.

The study's controllable factors and a respond factor were identified and listed. Temperature, stirring time, H_2SO_4 concentration, and the proportion of eucalyptus tissue and H_2SO_4 are the variables under control. The environmental temperature is important in the production of amorphous cellulose because the dissolution reaction between eucalyptus tissue and H_2SO_4 is good at low temperatures. Stirring time is another important controllable factor to investigate because it is directly related to activities along the production plan. Knowing the exact time period for each activity is useful for production planning. The concentration of H_2SO_4 is chosen based on previous research. Because it is related to production costs, the ratio of eucalyptus tissue and H_2SO_4 must be precisely set. Amorphous cellulose yield is the respond factor. After obtaining the cellulose-H2SO4 solution, GO will be added to it. The cellulose-H_2SO_4-GO solution will be placed in a dropping machine, and the dropping process will begin. Dropping rate, cellulose-H_2SO_4 solution portion amount to GO, gap between dropping mouth and water column, and injection head size are all controllable factors in the dropping process. The size of the ACGOHS bead is the respond factor.

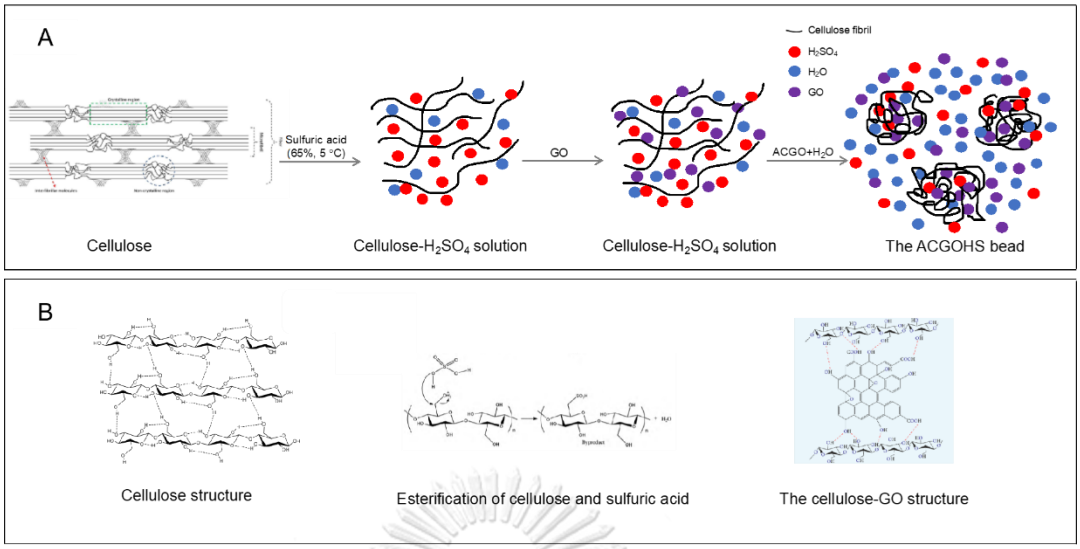


Figure 3.3 Schematic drawing of the (A) ACGOHS bead regeneration and (B) cellulose, esterification reaction and cellulose-GO chemical structure [26, 61]

Sulfuric acid destroys the hydrogen bonding of cellulose that occurs between the structures (some sulfuric acid reacts with cellulose via esterification reaction), and the completed reaction can be seen as the solution's color becoming transparent. Following that, GO was incorporated into the solution. Some GO was inserted between the cellulose ribbon gap, and some GO reacted with cellulose functional groups. Finally, as an anti-solvent, water was used. Because cellulose is insoluble in water, when the ACGOHS solution is dropped into water. The cellulose that was embedded by GO was formed into beads, and some H_2SO_4 was removed.

3.2.2 Validation stage

Validation stage consists of 4 steps including characterization, adsorption capacity, adsorption mechanism and recovery stage.

3.2.2.1 Characterization

Characterization research focused on the ACGOHS and amorphous cellulose beads. Images from the transmission electron microscope (TEM) and scanning electron microscope (SEM) was used for surface examination. To investigate functional groups, Fourier transform infrared spectroscopy (FTIR) was

used. The purity of the product was investigated using the Raman spectra, and the Brunauer-Emmett-Teller (BET) surface area was also investigated [8]. Additionally, the elemental composition of the surface was studied using X-ray photoelectron spectroscopy (XPS), and the pore volume and pore-size distribution was studied using the Barrett-Joyner-Halenda (BJH) method [27].

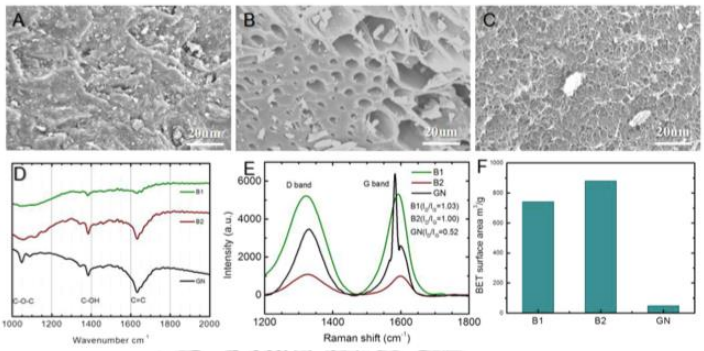


Figure 3.4 Example of two biochar and graphene characterization, (A–C) SEM images; (D) FTIR; (E) Raman shift; (F) surface area [8]

3.2.2.2 Adsorption capacity

The antibiotics chosen for the experiment were tetracycline (TET), ciprofloxacin (CIP), and norfloxacin (NOR), which are the most commonly prescribed at Mahasarakam hospital and the most commonly detected in wastewater effluent at Songkla hospitals. Furthermore, the average TET, CIP, and NOR removal efficiency for Songkla hospitals was 98.3%, 70.5%, and 63.5%, respectively [39, 65]. The adsorption equilibrium time was plotted, showing the antibiotic concentration change as a function of time [8]. The removal percentage (R%) and the amount of antibiotics adsorbed (qe) was also computed. In order to explain the adsorption process, the experiment data was described using the adsorption kinetics model, which consists of pseudo first and second order kinetic models. The Langmuir and Freundlich models was used to describe the adsorption equilibrium.

3.2.2.3 Adsorption mechanism

The adsorption mechanism was visualized via schematic diagram.

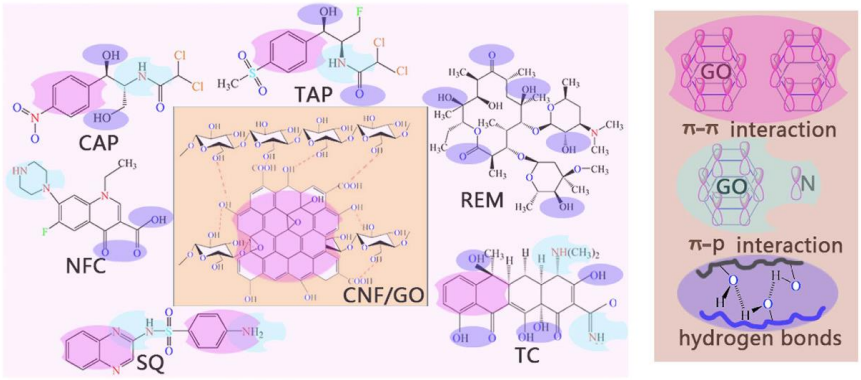


Figure 3.5 Example of adsorption mechanism visualization [27]

3.2.2.4 Effect of pH, temperature, dosage of sorbent and initial concentration of adsorbate

The Effect of those factors was shown by the graph between the factor and removal percentage (R%).

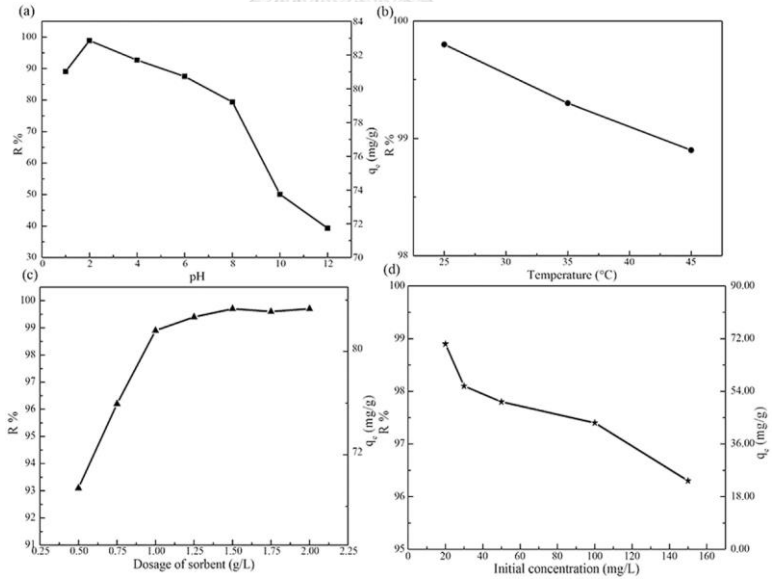


Figure 3.6 Example graphs of factors' effect [27]

3.2.2.5 Recovery stage

The ACGOHS bead will be recovered in order to be practice usage, detailed with be descried in the latter chapter.

3.3 Phase 3: Mass scale production plan

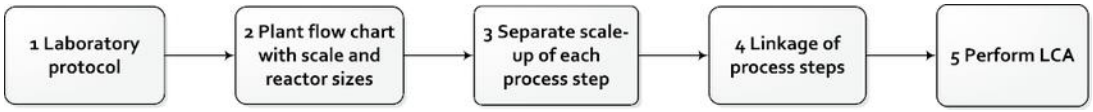


Figure 3.7 The mass scale procedure [10]

Topic 3.1 implemented the lab-scale production protocol, while Topic 3.2 implemented the ACGOHS bead prototype. However, parameters such as reaction temperature, yield, cellulose and GO portion, and so on are not solid and must be transformed to solid after the experiment. The ACGOHS bead will be scaled up from lab to pilot scale and then to near commercial scale. To meet the mass scale production goal, the plant flow chart and reactor sizes were studied and described in detail in the following chapter. This chapter used operation research and/or design of experiments (DOEs) theory to study parameters in order to optimize the scale-up plan. Furthermore, sufficient raw material sources were required to feed into the system, which suppliers can explore later. Bleached eucalyptus, sulfuric acid, and graphene oxide were used as input materials in the process.

3.4 Phase 4: Commercialization plan

The commercialization plan was divided into two sections: market analysis and financial planning. PEST analysis, business model, SWOT, competitive landscape and market size, STP strategy, marketing mix (4P), challenge and opportunity, intellectual property, operation plan, and market survey to shrimp farmers (customer demand questionnaire) are all part of the market analysis studies. Start-up costs, funding strategies, production plans, sales plans, selling prices and unit costs, operating costs, and financial plans were all studied in financial plans.

Chapter 4
Optimized ACGO bead fabrication protocol and characterization

The bead form is chosen to be fabricated after the optimized AC and ACGOHS prototypes were obtained. The researcher renamed AC and ACGOHS from previous chapters to AC and ACGO bead.

As a result, the goal of this chapter is to implement a standard protocol for producing AC and ACGO beads. After obtaining the prototype bead and the optimized production protocol, the beads were characterized. Image J was used to measure size distribution, Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy (RAMAN), thermal gravimetric analysis (TGA), X-ray diffraction (XRD), and scanning electron microscopy (SEM) were used to characterize the product. As a result, this chapter is divided into two sections: protocol development and characterization.

As shown in Figure 4.1, the ACGO bead fabrication protocol was divided into two stages: preparation of AC and ACGO gels and preparation of AC and ACGO beads. The preparation of AC and ACGO gels stage includes raw material preparation and cellulose dissolution, while the regeneration stage includes ACGO bead fabrication and cleaning.

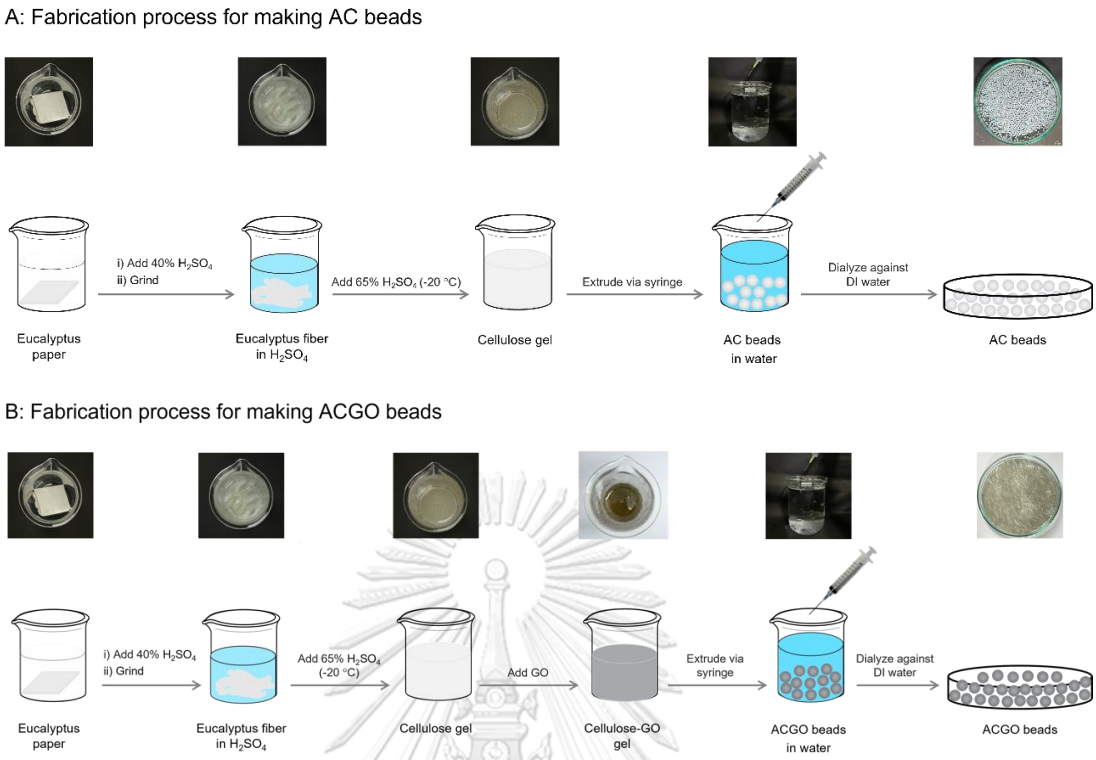


Figure 4.1 Fabrication process of (A) AC and (B) ACGO beads

4.1 Preparation of raw material experiment

The challenge of this stage is to prepare eucalyptus paper for the dissolution stage, in which the prepared material must be wet and small in size to overcome existing methodology that uses mechanical force to prepare material, such as a grinding machine and a fruit blender [47]. Mechanical force has the disadvantage of consuming a lot of energy and causing the production process to stop. To overcome the limitations of high energy consumption and a discontinuous production process, the researcher proposed using 40%wt H_2SO_4 (RT) instead of mechanical force to prepare the raw material for the dissolution stage. As a result, instead of mechanical force, the first set of 40%wt H_2SO_4 (RT) was used in the preparation process.

The following factors are taken into account when preparing material with 40%wt H_2SO_4 (RT): amount, time, and temperature. As a result, an experiment was devised to determine the optimal amount and temperature of the first batch of H_2SO_4 in terms of the quality and cost effectiveness of prepared eucalyptus paper. The evaluation of the raw material preparation experiment will be done using a ligure scale based on the wetness and size of the eucalyptus paper after the first set of

H_2SO_4, as shown in Figure 4.2C and D, and the score is defined as shown in Figure 4.3. As a result, the entire experiment was split into four parts. The goal of the first experiment was to find the best H_2SO_4 solution for the first set, and the goal of the second experiment was to find the best H_2SO_4 solution for the second set. The third experiment looked into the production of AC and ACGO beads. The final (fourth) experiment determined the time required to dialyze an ACGO bead from pH = 2 to the same pH as DI water.

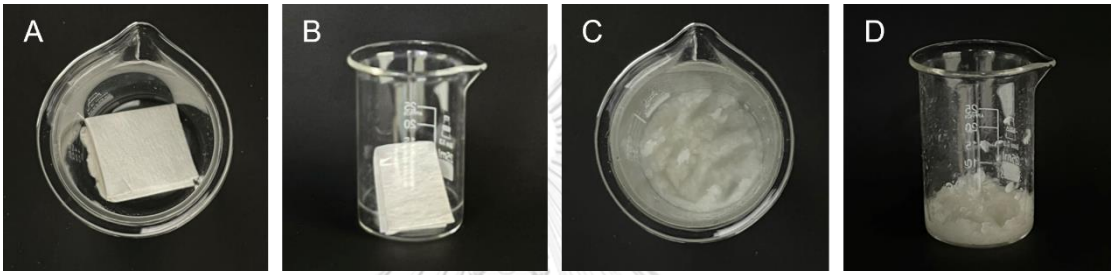


Figure 4.2 Preparation of material (A) top view of eucalyptus paper in the beaker, (B) side view of eucalyptus paper in the beaker, (C) top view of eucalyptus paper filled with 1st set of H_2SO_4, and (D) side view of eucalyptus paper filled with 1st set of H_2SO_4

4.1.1 First experiment: Optimal concentration and amount of the first set of H_2SO_4

1. The amount of H_2SO_4 in the solution (x; 30, 40, or 50%wt H_2SO_4) was taken into account as the independent variable. The independent variable (x) was established at three levels of 30, 40, and 50%wt H_2SO_4, with three distinct H_2SO_4 consumption amounts of 3, 4, and 5 mL, respectively, in each level.

2. The dependent variable is the eucalyptus characteristic (y; the score was evaluated by having a total score of 9).

3. The controllable variables were temperature (environment temp), contact time (1 min) and cellulose amount (1 g).

4. Each set of experiment was done in triplicate.

The result was rated from 1 to 3, with 3 as the highest score. The meaning of each score level is listed as following:

1. H_2SO_4 solution cannot seep through the eucalyptus fiber or cover over making the fiber hard.
2. Medium and dry pieces
3. Very small and wet pieces

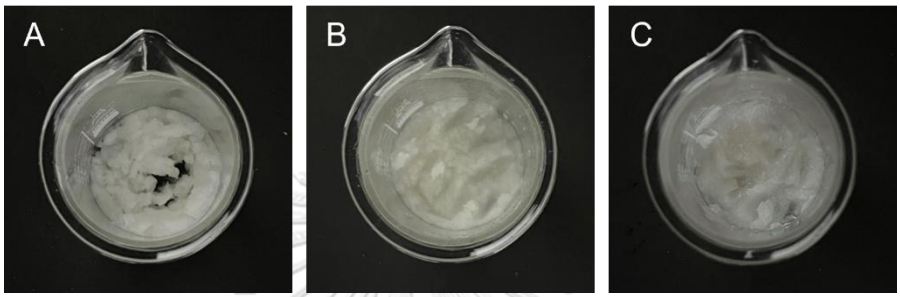


Figure 4.3 Characteristic of score 1, 2 and 3

Methodology:

Table 4.1 30 %wt H_2SO_4

Exp. no.	H_2SO_4 amount (mL)	Score	Score	Score	Total score (9)
1-3	3	1	1	1	3
4-6	4	1	1	1	3
7-9	5	1	1	1	3

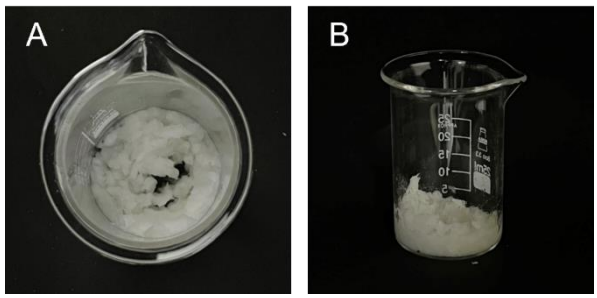


Figure 4.4 Characteristic of eucalyptus after 30 %wt H_2SO_4 preparation

Table 4.2 40 %wt H_2SO_4

Exp. no.	H_2SO_4 amount (mL)	Score	Score	Score	Total score (9)
10-12	3	2	2	2	6
13-15	4	3	3	3	9
16-18	5	3	3	3	9

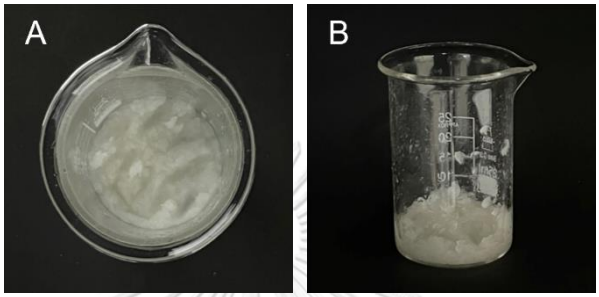


Figure 4.5 Characteristic of eucalyptus after 40 %wt H_2SO_4 preparation

Table 4.3 50 %wt H_2SO_4

Exp. no.	H_2SO_4 amount (mL)	Score	Score	Score	Total score (9)
19-21	3	2	2	2	3
22-24	4	3	3	3	9
25-27	5	3	3	3	9

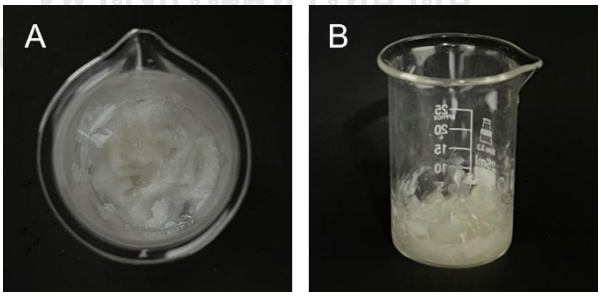


Figure 4.6 Characteristic of eucalyptus after 50 %wt H_2SO_4 preparation

Conclusion

Within 1 minute, 4 and 5 mL of 40%wt H_2SO_4 obtained the highest score (9) while all quantities of 3 mL of 30%wt and 50%wt H_2SO_4 obtained the lowest score (3). 30% H_2SO_4 could not seep through eucalyptus paper, whereas 50%wt H_2SO_4 covered eucalyptus paper, posing a dissolution difficulty. As a result, the 4 ml of 40%wt H_2SO_4 was chosen as optimal because it has the highest score and is the most cost effective.

4.2 Cellulose dissolution

The second experiment is cellulose dissolution, which showed three significant stages of characteristic transformation as shown in Figure 4.7. In summary, the prepared eucalyptus paper was transformed to a joke state, then to a gel stage, and finally to a transparent gel that is ready to be regenerated. GO was combined into the transparent gel during the transparent gel stage (D), transforming it to ACGO gel (E).

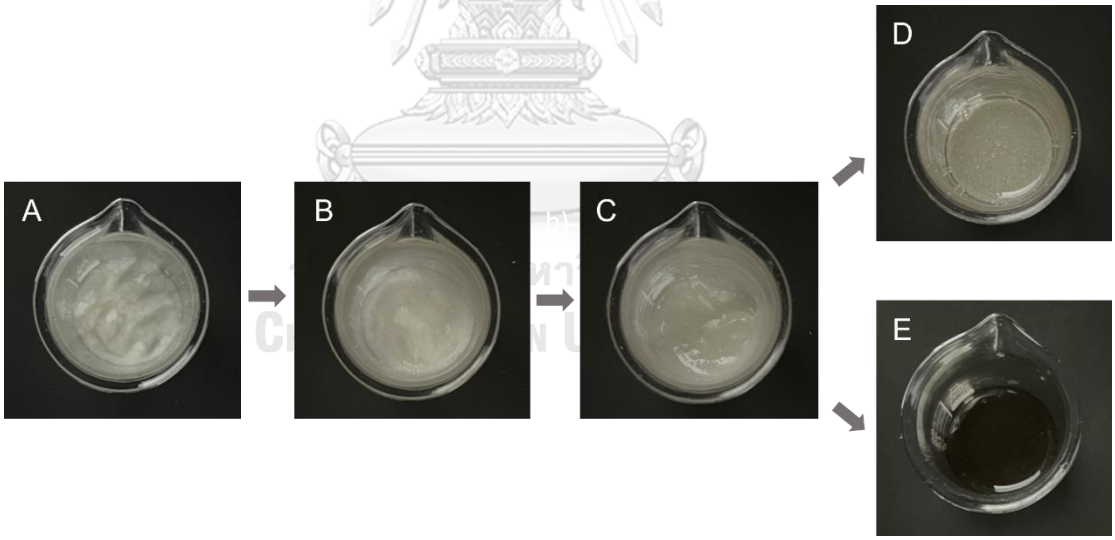


Figure 4.7 Cellulose dissolution process (A) prepared eucalyptus paper, (B) joke stage, (C) gel stage, (D) transparent gel and (E) ACGO gel

In this stage, 65 %wt H_2SO_4 was the solvent selected because according to [47] the lowest concentration to dissolve high molecular weight cellulose was 64 %wt H_2SO_4. Therefore, in this experiment 65 %wt H_2SO_4 was chosen to be the solvent. However, the optimal amount, dissolution time and temperature are still questionable.

Thus, the second experiment on the optimal amount of solvent, dissolution time and temperature were conducted.

Second experiment: Dissolution experiment

This experiment is a continuation of the first because the prepared eucalyptus paper from the first experiment was dissolved under different conditions. The primary objective of this experiment was to create transparent gel for bead fabrication. The following are the experiment's factors:

The independent variable (x): 65 %wt H_2SO_4 amount, environment temperature (Room temperature and -20°C)

The dependent variable (y): Transparent level

Controllable variables: -20 °C pre-cooled 65 %wt H_2SO_4, stirring method, 1 g eucalyptus paper, contact time (6 min)

The score was rated in two levels which are 1 and 2.

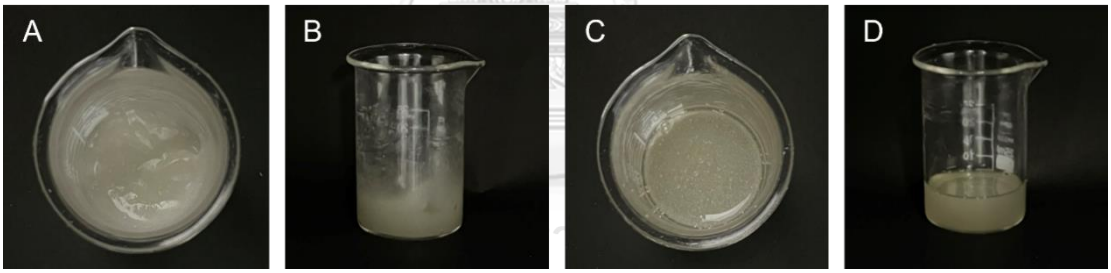


Figure 4.8 (A), (B) score is 1 and (C), (D) score is 2

Methodology:

In this experiment, the researcher expected to obtain the transparent gel with the lowest energy consumption. The experiments were designed for Type 1 (65 %wt H_2SO_4 at room temperature) and Type 2 (65 %wt H_2SO_4 at -20°C as solvent).

Table 4.4 Type 1: Environment temperature: room temperature

Exp. no.	65 %wt H_2SO_4 amount (mL)	Score	Score	Score	Total score (6)
1-3	3	1	2	2	5
4-6	4	2	2	2	6
7-9	5	2	2	2	6

Table 4.5 Type 2: Environment temperature: -20°C

Exp. no.	65 %wt H_2SO_4 amount (mL)	Score	Score	Score	Total score (6)
1-3	3	1	1	1	3
4-6	4	2	2	2	6
7-9	5	2	2	2	6

Conclusion

The highest score (6) was obtained with 4 mL of Type 1 and 2 environment conditions. Type 1 was chosen because it had the highest dissolution score and was the most cost effective when compared to type 2, which required energy to reduce the temperature to -20 °C. As a result, for the bead fabrication experiment, 4 mL of 65%wt H_2SO_4 would be used. Given that the bead strength for the third experiment may have an effect on the environmental temperature (RT and -20 °C) of the second experiment, the optimum conditions of both Type 1 and Type 2 from this experiment would be used for strength testing in the third experiment before deciding whether Type 1 or Type 2 would be used for bead fabrication.

4.3 Bead fabrication

AC and ACGO beads were fabricated in two series. The raw material for the fabrication of the AC and ACGO beads comes from the third experiment, 4 mL of transparent gel (RT and -20 °C), which are the optimized solutions. The reason for not using only transparent gel (RT) was the possibility of affecting the percentage of unbreakable beads. As a result, this experiment was divided into two sections. The first section consisted of fabricating AC beads from optimal Type 1 and 2, followed by an evaluation of breakable percentage. The second section was to make ACGO

beads from the Type with the lowest breakable percentage from the first section after comparing the breakable percentages of two GO proportions.

Bead Fabrication methodology

The ACGO gel was loaded into a 22-gauge syringe and droplet-extruded into a beaker containing 500 mL of deionized (DI) water. A white cellulose bead (AC bead) was immediately formed, as shown in Figure 4.9A. When the ACGO gel was droplet-extruded into DI water, an ACGO beads were generated as shown in Figure 4.9B.

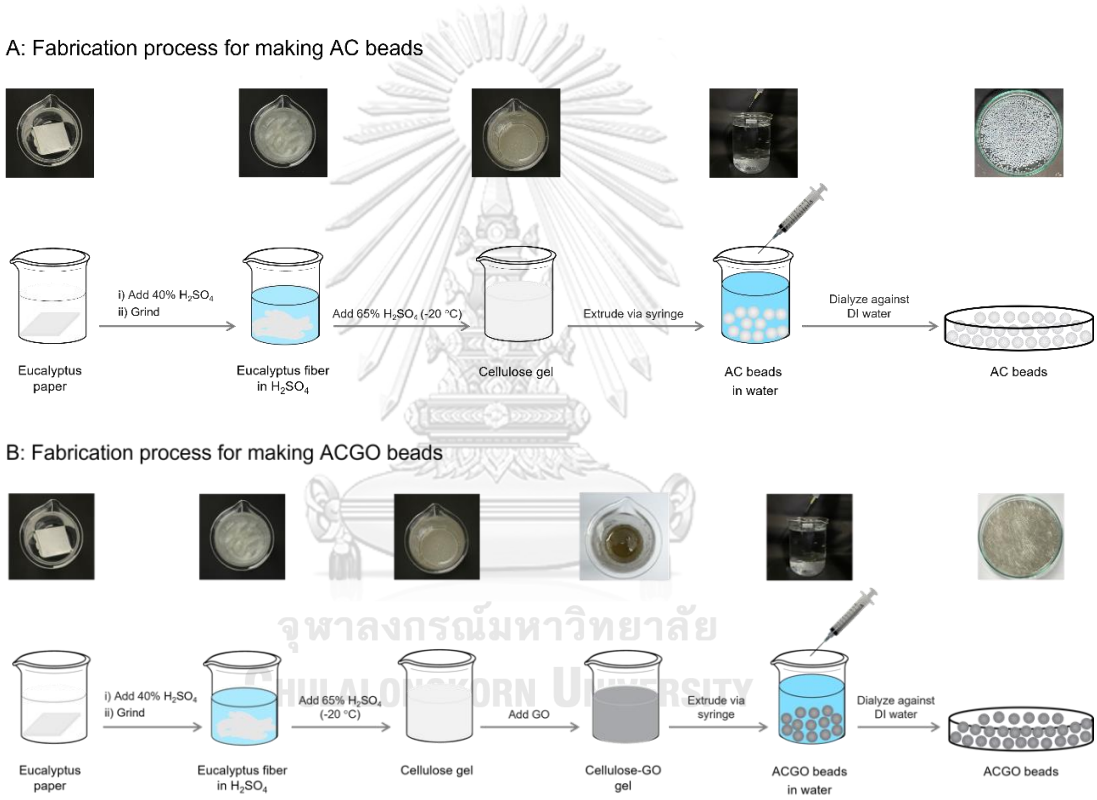


Figure 4.9 Fabrication process for making (A) AC and (B) ACGO beads

4.3.1 AC bead experiment and unbreakable bead percentage

The purpose of this experiment is to measure the strength of AC and ACGO beads by gently touching a bead with a stirring rod. The unbreakable percentage of AC beads is shown in Table 4.6, while the unbreakable percentage of ACGO beads is presented in Table 4.7. The following are the variables used in this experiment.

The independent variable: Cellulose transparent gel (Type 1 and 2)

The dependent variable: % Unbreakable bead

Controllable variable: Dropping distance (6 cm), water level (500 mL of DI water in 500 mL beaker), antisolvent (precipitation agent) temperature is RT, 22-gauge needle size, softly touch by a stirring rod.

Table 4.6 Number of unbreakable beads using 300 AC pure beads

Exp. no.	Gel type	Unbreakable bead amount	Unbreakable bead amount	Unbreakable bead amount	% Avg. unbreakable
1-3	RT	15	10	20	5%
4-6	-20 °C	3	2	2	0.78%

Conclusion

The RT gel (Type 1) obtained higher unbreakable bead percentage. Thus, it was chosen to be the gel for the next experiment in ACGO bead fabrication (combining with GO)

4.3.2 ACGO bead fabrication experiment

GO was added to the transparent gel (Type 1) in this experiment, but the appropriate amount of GO was still debatable. Because of the well-dispersed nature of GO in cellulose, two amounts (0.5 and 1 mL) of GO were added to the transparent gel. The percentage of unbreakable beads was used to determine which amount of GO would be a good representative for the optimal protocol. The following are the variables used in this experiment.

The independent variable (x): ACGO proportion

The dependent variable (y): % Unbreakable bead

Controllable variables: Dropping distance (6 cm), water level (500 mL of DI water in 500 mL beaker), antisolvent (precipitation agent) temperature is RT, 22-gauge needle size.

Table 4.7 Number of unbreakable of 300 ACGO beads

Exp. no.	Euca (g) : GO (mL)	unbreakable bead amount	unbreakable bead amount	unbreakable bead amount	% Avg. unbreakable
1-3	1:0.5	290	294	290	97
4-6	1:1	292	294	296	98

ACGO beads in different media, including acid, base, and water, provide different stability. Amorphous cellulose (AC) has a hydroxyl group. In addition, graphene oxide (GO) contains epoxy groups, hydroxyl groups, carboxyl groups, and carbonyl groups. These hydrophilic groups impart surface activity and wettability, and their electrostatic repulsion characteristics facilitate the stable dispersion of GO in water or alkaline solution. So, the ACGO beads in water and base maintain the original state better than the base and acid solution [43] While ACGO beads in acidic conditions cause poor retention. Because the acid could dissolve cellulose and break hydrogen bonds in ACGO, the mechanical properties of ACGO are reduced [69, 70].

Conclusion

The percentages of unbreakable beads out of 300 beads prepared using the combination of eucalyptus paper (g) and GO (mL) (1:0.5 and 1:1) were 97% and 98%, respectively, which exceeded 95%. Based on cost effectiveness, the optimum protocol for ACGO bead fabrication was the 1:0.5 ratio of eucalyptus paper (g): GO (mL) and would be used for ACGO bead fabrication.

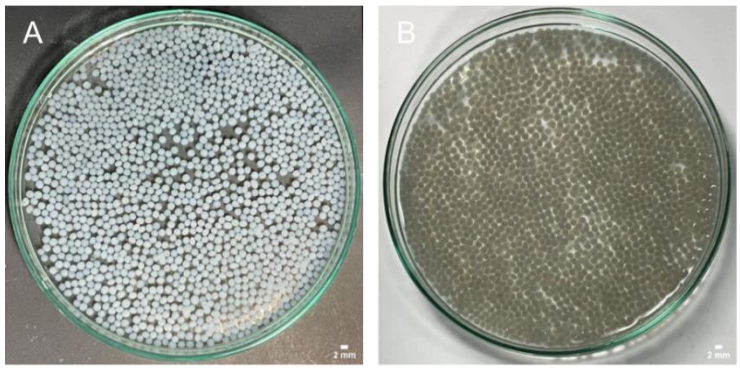


Figure 4.10 (A) AC pure beads, (B) ACGO beads prototype

4.4 Cleaning experiment

The pH level of the beads after the regeneration process was 2, which was far too acidic for application. As a result, the pH was adjusted to achieve the pH of DI water via the dialysis process. AC and ACGO beads were used in the pH adjustment experiment during the process.

Dialysis process methodology

Dialysis was performed on the beads using 1000 mL of DI water. Every 24 hours, DI water was replaced until the pH reached that of DI water (pH=5). The following are the variables used in this experiment. The independent variable (x): Day amount

The dependent variable (y): pH of beads

Controllable variables: 24-hour water changing, water temperature (RT), 1000 mL of water in 1000 beaker

AC bead cleaning experiment

Table 4.8 AC Bead cleaning experiment

Exp. no.	pH of day 1	pH of day 2	pH of day 3	pH of day 4	pH of day 5	pH of day 6	pH of day 7	Conclusion
1	2	3-4	5-6	5-6	5-6	5-6	5-6	Day 3
2	2	3-4	5-6	5-6	5-6	5-6	5-6	Day 3
3	2	3-4	5-6	5-6	5-6	5-6	5-6	Day 3

AC (1g) : GO (0.5 mL) bead cleaning experiment

Table 4.9 AC (1g) : GO (0.5mL) bead cleaning experiment

Exp. no.	pH of day 1	pH of day 2	pH of day 3	pH of day 4	pH of day 5	pH of day 6	pH of day 7	Conclusion
1	2	3-4	5-6	5-6	5-6	5-6	5-6	Day 3
2	2	3-4	5-6	5-6	5-6	5-6	5-6	Day 3
3	2	3-4	5-6	5-6	5-6	5-6	5-6	Day 3

Conclusion bead cleaning experiment

It was determined that the pH adjustment by dialysis took 3 days to raise the pH of AC and ACGO beads from 2 to the same level as DI water (pH = 5).

Grand Summarization

Preparation of AC and ACGO gels

For the preparation of AC and ACGO gel, two sets of sulfuric acid solutions were used: 40%wt H2SO4 (RT) and 65%wt H2SO4 (pre-cooled to -20°C). In a 25 mL beaker, 1 g of eucalyptus paper was placed, and 4 mL of 40%wt H_2SO_4 was poured into the beaker. A stirring rod immediately broke down the paper into suspended fibers. The entire procedure took about 1 minute. Following that, 65%wt H_2SO_4 was gradually added to the suspension while mixing it with a glass rod until a transparent cellulose gel was obtained. The gelatinization of H_2SO_4 was done in an ice bath. The entire procedure took about 6 minutes. To produce the cellulose gel, 4 mL of cold 65%wt H_2SO_4 were used. To produce a cellulose gel with graphene oxide, 2 mL of 10% GO in water was added to the gel and thoroughly mixed for 1 minute with a stirring rod. Finally, two types of cellulose gel were produced: cellulose gel in cold sulfuric acid (AC gel), as shown in Figure 4.10A, and cellulose-GO gel in cold sulfuric acid (ACGO gel), as shown in Figure 4.10B.

Preparation of AC and ACGO beads

The ACGO gel was loaded into a 22-gauge syringe and droplet-extruded into a 500-mL beaker containing DI water. As shown in Figure 4.10A, a white cellulose bead (AC bead) was formed immediately. Figure 4.10B shows an ACGO bead formed after droplet-extruding the ACGO gel into DI water. The beads were then dialyzed against 1000 mL of DI water. Every 24 hours for 3 days, DI water was replaced until the pH reached that of DI water (pH=5).

4.5 Bead characterization

The AC and ACGO beads were fixed onto a glass slide and then photographed. Size distribution of 200 beads were analyzed by Image J software (Image J bundled with Java 1.8.0_172, Bethesda, Maryland, USA). AC and ACGO beads were dried

with vacuum drying prior to analysis by FTIR, Raman, TGA, XRD and SEM techniques. FTIR spectra were measured on a Nicolet iS5 FTIR spectrometer with iD7 ATR accessory (Thermo Fisher Scientific Inc., Waltham, Massachusetts, USA) in the range of 400-4000 cm^{-1} by averaging 32 co-addition scans at a resolution of 4 cm^{-1}. Raman spectra were recorded from 300 to 3000 cm^{-1} using a Raman microscope (Thermo Scientific DXR3 Raman microscope, Thermo Fisher Scientific Inc., Waltham, Massachusetts, USA) with a 532 nm excitation laser via a 100x objective lens. Thermal gravimetric analysis (TGA) was conducted by a thermogravimetric analyzer (PYRIS-1 TGA, Shelton, USA) in nitrogen atmosphere. The temperature program was 30-700°C with 20°C/min heating rate. X-ray diffraction (XRD) patterns were acquired using an X-Ray diffractometer (Bruker AXS Model D8 Discover, Billerica, Massachusetts, USA) operated at 40 kV and 40 mA with Cu K_α radiation. The diffraction angle was in the range of 1° to 80° with a scanning speed of 2.5°/min. The morphologies of eucalyptus paper, AC and ACGO bead were observed by a scanning electron microscope (JEOL - Model JSM-6510LV Series, Tokyo, Japan) with an accelerating voltage of 15 KV under high vacuum mode.

4.5.1 Size distribution

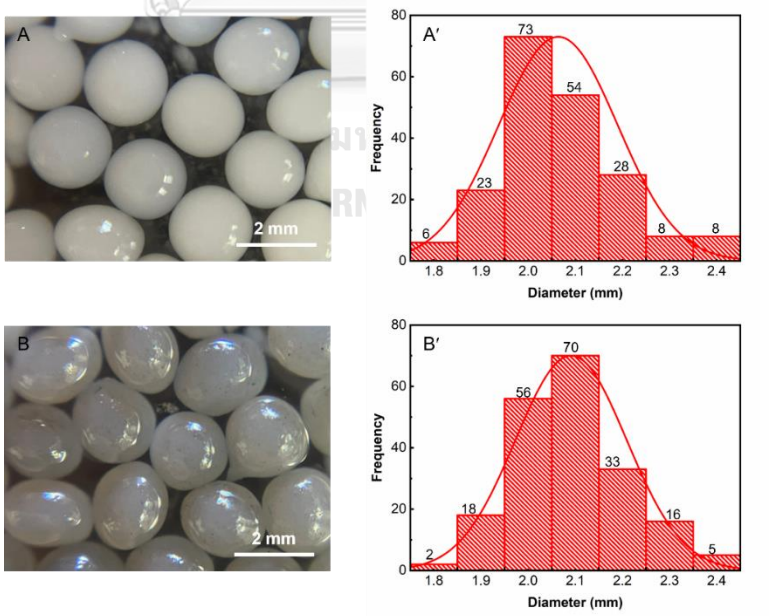


Figure 4.11 Photographic images of (A) AC and (B) ACGO beads and their corresponding histograms

The AC and ACGO beads were both quasi-spherical with AC beads having white (Figure 4.11A) while ACGO beads having light-brown colors (Figure 4.11B). The light-brown color of ACGO beads was due to the embedded GO in the regenerated amorphous cellulose. The histograms in Figure 4.11 indicated that the AC beads had mean diameter (d_{AC}) of 2.11 ± 0.13 mm while that of ACGO beads (d_{ACGO}) were 2.14 ± 0.12 mm.

4.5.2 FTIR and Raman spectra

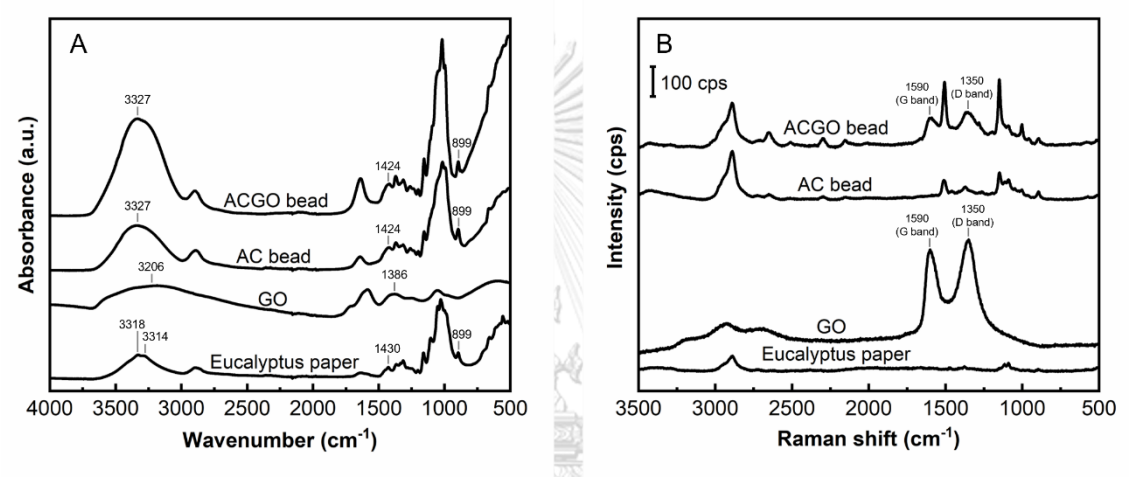


Figure 4.12 (A) FTIR and (B) Raman spectra of eucalyptus paper, GO, AC and ACGO beads

Cellulose I and II were the most common celluloses in which cellulose I was in the native form while cellulose II was in the swollen form after treatment of cellulose I [44]. The FTIR spectra of eucalyptus paper, AC, and ACGO beads are shown in Figure 412A. After the eucalyptus paper was gelatinized and regenerated into AC and ACGO beads, no new peak appeared. However, three notable peak shifts confirmed that cellulose I was successfully transformed to cellulose II following the regeneration process. Firstly, the peaks at 3318 and 3314 cm^{-1} (OH stretching of intra-molecular H-bonding at O(3)H···O(5) in cellulose I) of eucalyptus paper shifted to 3327 cm^{-1} (OH stretching of intra-molecular H-bonding at O(3)H···O(5) of cellulose II). The OH stretching region became broader after the regeneration process. Secondly, the peak at 1430 cm^{-1} (CH_2 scissoring mode of C(6) in cellulose I) of eucalyptus paper decreased in intensity and shifted to 1424 cm^{-1} (CH_2 scissoring mode

of C(6) in cellulose II). This shift indicated the disappearance of crystalline structure of cellulose I as its transformed to the amorphous structure of cellulose II. Lastly, the peak intensity at 899 cm^{-1} (C-O-C stretching symmetric of glycosidic linkage of cellulose II) increased. These spectroscopic changes, which were directly associated with molecular structures, confirmed that the inter- and intra-molecular H-bonds in cellulose I structure had disappeared and new arrangement of disordered H-bonding in cellulose II had formed [47, 71-73]. Although FTIR spectra did not show characteristic peaks of GO in ACGO bead but Raman spectra clearly revealed characteristic peaks of GO (Figure 4.12B). Two strong peaks at 1350 and 1590 cm^{-1} of the ACGO curve were assigned as D and G bands, respectively [74]. The intensity ratio (I_D/I_G) of 1.3 indicated abundance of oxygen-containing functional groups on GO which promoting its interaction with OH groups in amorphous cellulose (as depicted in Figure 4.12B). The observed spectroscopic information confirmed that GO was successfully embedded in amorphous cellulose structure.

4.5.3 TGA and DTG

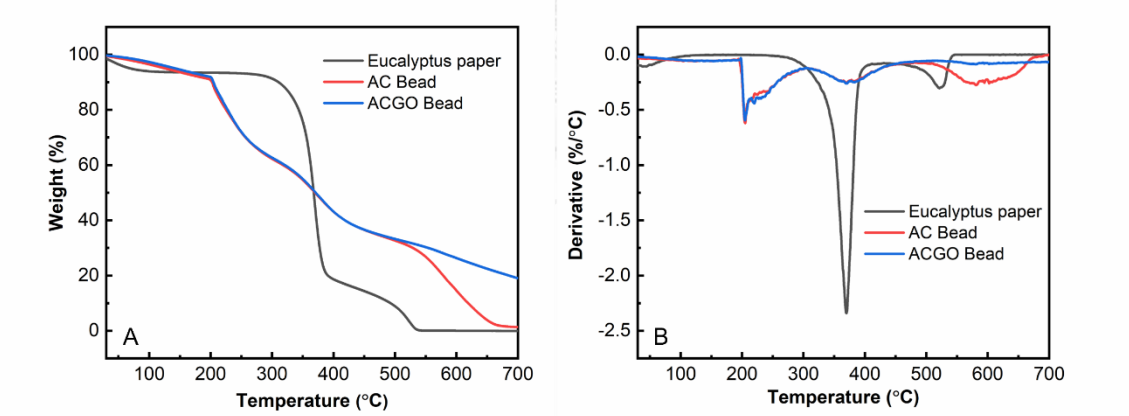


Figure 4.13 (A) TGA and (B) DTG curves of eucalyptus paper, AC and ACGO beads

The thermal activities of eucalyptus paper, AC and ACGO beads were studied by thermal gravimetric analysis (TGA, Figure 4.13A) and derivative weight loss analysis (DTG, Figure 4.13B). All samples showed small weight loss below 100°C due to evaporation of water [62]. At 200°C to 400°C, the decomposition of all samples was attributed to the depolymerization and decomposition of cellulose [75]. The thermal degradation of eucalyptus paper started at the onset temperature (T_{onset})

of 300°C and reached peak temperature (T_{peak}) at 380°C. Both the AC and ACGO beads were less thermally stable than the eucalyptus paper with an approximate T_{onset} of 200°C since they had higher portion of amorphous cellulose [62]. In addition, the small peak at 500°C was attributed to trace lignin decomposition [76]. A 20% char yield of ACGO beads at 700°C was attributed to the residual GO as it decomposes at a higher temperature (~850°C) [33].

4.5.4 XRD patterns

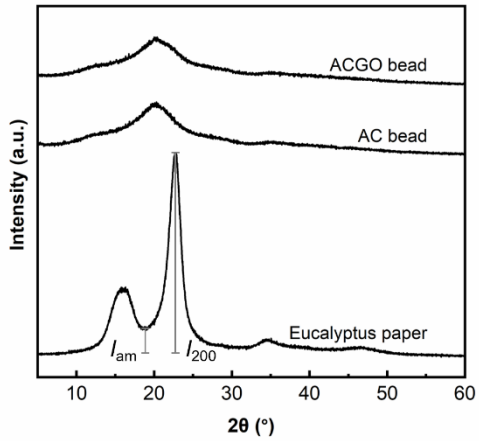


Figure 4.14 XRD patterns for eucalyptus paper, AC and ACGO beads

XRD patterns of eucalyptus paper, AC, and ACGO beads were shown in Figure 4.14. The patterns confirmed the transformation of cellulose I to cellulose II up on gelatinization and subsequent regeneration of the semicrystalline eucalyptus paper. The XRD pattern of eucalyptus paper showed typical diffraction peaks at 17.1° and 22.7° corresponding to cellulose I [51-53]. The crystallinity index (CI) of 83% , calculated from the XRD pattern in Figure 4.14 using Segal formular [53], suggested that the employed eucalyptus fiber was a semicrystalline cellulose with high portion of cellulose I.

XRD patterns of AC and ACGO beads in Figure 4.14, however, did not show any diffraction signature of semicrystalline cellulose at 17.1° or 22.7°. The XRD patterns of AC and ACGO bead, on the other hand, showed a single broad peak at 21.9°, attributing to cellulose II or amorphous cellulose [7]. Our observation is similar to those report by Park et al. [54]. The CI% of AC and ACGO bead could not

be calculated due to a completed transformation of semicrystalline cellulose to amorphous cellulose under the gelatinization and regeneration process.

4.5.5 SEM

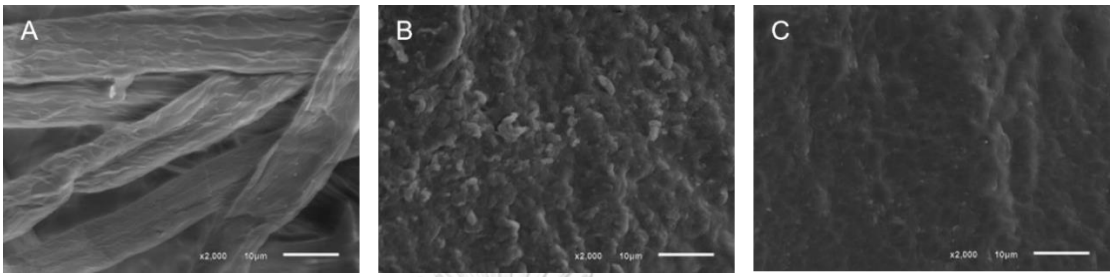


Figure 4.15 SEM images of (A) eucalyptus paper, (B) AC and (C) ACGO beads

SEM images of eucalyptus paper, AC and ACGO beads were shown in Figure 4.15. Figure 4.15A illustrated that the eucalyptus paper consisted of fibers with diameters of 10-15 μm. The SEM image of AC beads (after drying, Figure 4.15B) revealed a rough surface while that of ACGO beads revealed a smoother surface (Figure 4.15C). The interaction of the added GO with the OH groups in amorphous cellulose may result in a smoother surface of ACGO beads as the surface of GO is abundant in hydrophilic groups [36, 51, 52, 55]. ACGO composites were applicable in products such as adsorbent [33, 34], film [7], and bead [40]. It indicates that ACGO composites have potential to be in industries such as films and water treatment.

Chapter 5
Scaling-up fabrication plan for ACGO bead

This chapter presents the plan for scaling-up production after obtaining the optimized protocol for fabricating ACGO beads (from Chapter 4). The plan will be illustrated by describing the scaling-up plant design, including whether it is feasible for management functions, safety, cost-effectiveness, and the possibility of future scaling-up. Furthermore, the pilot plant design will be tailored to the specific methodology of ACGO bead fabrication.

The following are important issues to consider when scaling up ACGO bead fabrication.

- Production quantity per day
- Production time and rate per day
- Scaling-up process
- The pilot plant design for the pilot production scale

5.1 Production quantity per day

The expected production quantity per day is divided into two scales which are the pilot scale and the near commercialization scale. The factor that separates the two scaling-up scales is the amount of ACGO gel per day.

The water quantity used in a shrimp farm for one crop of shrimp (size 6.25 rai) is 12,000,000 L, according to Table 6.6. As shown in Table 6.6, the researcher chose 12,000,000 L of water in shrimp farming as a representative of water quantity used in the shrimp farm. As a result, the optimal number of ACGO beads must be proportional to the size of the shrimp farm. However, due to the size of the market's reactors, the expected fabrication quantity of ACGO gel per day for the pilot and near commercialization scales is 510 and 2,550 L per day, respectively.

The usage amount from the laboratory scale will be used as the starting point for the initial material amount of the pilot and near commercialization scale, as shown in Table 5.1, to estimate the amount of material for the pilot and near commercialization scale.

The scaling-up strategy is divided into pilot and near-commercialization scales based on the fabrication quantity of ACGO gel. According to the laboratory experiment, 1 g of eucalyptus paper requires 4 mL of both 40%wt and 65%wt H_2SO_4 and 0.5 mL of GO, yielding a total volume of ACGO gel of approximately 8.5 mL. Table 5.1 shows the initial raw materials for ACGO gel fabrication at the laboratory, pilot, and near commercialization scales.

Table 5.1 Raw material and its usage amount to fabricate ACGO beads for laboratory, pilot and near commercialization scale

Material	Quantity for laboratory scale	Quantity for pilot scale	Quantity for near commercialization scale
Eucalyptus paper	1 g	60 kg	300 kg
40 %wt H_2SO_4	4 mL	240 L	1,200 L
65 %wt H_2SO_4	4 mL	240 L	1,200 L
GO	0.5 mL	30 L	150 L
ACGO gel	8.5 mL	510 L	2,550 L
ACGO bead	300 bead	18,000,000 bead	90,000,000 bead

Table 5.1 shows that the laboratory, pilot, and near commercialization scales are expected to produce 300, 18,000,000, and 90,000,000 beads per day, respectively. The pilot scale necessitates the use of 60 kg of eucalyptus paper, 240 L of both 40%wt and 65%wt H2SO4, and 30 L of GO, whereas the near commercialization scale necessitates the use of 300 kg of eucalyptus. The expected ACGO gel quantity per day is calculated using the available reactor sizes on the market. After determining the quantity per batch of ACGO gel, the production rate per day must be determined.

5.2 Production time and rate per day

The scaling-up scale's production fabrication rate per day is initially calculated from the laboratory scale, but the scaling-up scale demonstration will focus solely on the pilot scale, as shown in Table 5.2. The laboratory scale can produce 300 ACGO beads in 15 minutes, which is equivalent to 9,600 ACGO beads per day (8 hour working time, one extrusion). With 100 extrusion machines, 9,600 ACGO beads

(0.272 kg) can be produced with 1 extrusion and 8 hours of working time. The pilot scale (18,000,000 ACGO beads) requires 1,875 extrusion machines per working hour, while the commercialization scale (90,000,000 ACGO beads) requires 9,375 extrusion machines per working hour. However, in practice, the number of extrusion machines will be limited to 100 units, and the pilot scales will require more time to fabricate 18,000,000 ACGO beads, which will take approximately 150 hours or 19 working days to produce. The strategy for reducing production time to less than 19 days may include increasing working hours per day and purchasing more extrusion machines.

Table 5.2 Production rate per day

Assumption	Laboratory scale (bead)	Quantity of ACGO bead (kg)	Production time (hr)
Expected ACGO bead quantity per batch	300	0.0085	0.25
Production quantity per day with 1 extrusion machine	9,600	0.272	8
Production quantity per day with 100 extrusion machines	960,000	27.2	8
Production quantity per day with 1,875 extrusion machines	18,000,000	510	8
Production quantity per day with 9,375 extrusion machines	90,000,000	2,550	8

5.3 Scaling-up process

The scaling-up plan flow is designed in accordance with the ACGO bead fabrication protocol depicted in Figure 5.1. The fabrication of ACGO beads is divided into three stages: ACGO gel preparation (1st stage), ACGO bead fabrication (2nd stage), and packaging (3rd stage). It is a semi-continuous process in which ACGO gel is prepared in order to feed material for ACGO bead fabrication.

Figure 5.1 shows how eucalyptus paper was dissolved to form a transparent gel. However, mixing transparent gel to GO and then fabricating ACGO beads batch by batch would limit production. Thus, a feasible scaling-up production plan would be to

dissolve a large amount of transparent gel and store it in a -20C refrigerator until it is fed into a production line. Due to its chemical properties, the transparent gel on the production list must be kept at room temperature for 10 minutes before being mixed with GO and fed into the bead fabrication machine.

In detail, because of the 10-minute RT standby, the gel will be less tough or will not freeze, making it efficient to combine AC gel with GO to make ACGO gel. Following that, ACGO gel will be fed into an extrusion machine and extruded into water (anti-solvent) before being changed to bead form. The cleaning process will then begin. After the ACGO beads are fabricated and the DI water container is full, the beads will be transferred to the customized basin to begin the dialysis process for three days (replace new water daily). After the dialysis process is completed, the beads will be collected in a large basin before the packaging process begins.

Figure 5.1 Flow of scaling-up plan

In Figure 5.1, eucalyptus paper was transformed into a transparent gel via a dissolution process, and the transparent gel was stored in the refrigerator while waiting to be fed into the production line. The gel in the refrigerator will be removed from the refrigerator and kept at room temperature for 10 minutes before being mixed with GO, then fed into the extrusion machine and finally extruded into DI water. The collected ACGO beads will be transferred to another specially prepared DI water basin for the dialysis process. Following the dialysis process, the ACGO beads will be transferred to a large basin that will be filled with DI water prior to the packaging process. The final ACGO bead package will include DI water and beads.

5.4 The pilot plant design for the pilot production scale

The pilot plant design is based on the fabrication of ACGO beads, as shown in Figure 5.2.

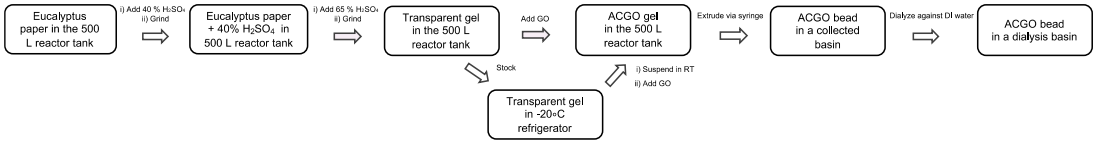


Figure 5.2 The ACGO bead scaling-up plan for the pilot scale [77]

Figure 5.2 depicts a pilot scale for the production of 510 L/day of ACGO gel. According to Table 5.2, the total amount of materials used for ACGO bead fabrication is 510 L, which includes the following amounts: 40%wt H_2SO_4 (240 L), 65%wt H_2SO_4 (240 L), and GO (30 L), which will be the first priority factor in determining reactor size. In the fabrication process, two reactor tanks are used. The first is a 500 L reactor tank, while the second is a 300 L reactor tank. The 500 L reactor tank is used in the preparation of eucalyptus paper, adding 40 and 65%wt H_2SO_4 for dissolution, and the other 500 L reactor tank will be used to mix the cellulose transparent gel and GO. The 300 L was chosen in this process because 500 L of the amorphous transparent gel cannot be mixed with GO at the same time without affecting the ACGO gel properties. The remaining cellulose transparent gel will be kept in the refrigerator until the next production call. After extruding 510 L of ACGO gel into bead forms, the machine will be stopped for a short rest. The following batch of ACGO gel will be fed into the extrusion machine. The ACGO beads will be collected in the DI water basin for the dialysis process before being transferred to the final basin after the dialysis process is completed, and finally with the packaging process. The pilot scale production (300 L) would be multiplied by 5 for the near commercial scale, which expects to have 1,500 L of ACGO gel per day.

Table 5.3 The required equipment for the ACGO bead fabrication for the pilot and near commercial scale [78]

No.	Equipment	Amount for pilot scale	Price per unit (THB)	Total price (THB)
1	500 L reactor tank	4	53,000	212,000
2	300 L reactor tank	5	30,000	150,000
3	-20°C refrigerator	2	57,000	114,000
4	Extrusion basin	10	800	8,000
5	Dialysis basin	10	800	8,000
6	Collected basin	10	800	8,000
7	Pump	100	1,000	100,000
8	Syringe	50,000	2	100,000
			Total	**700,000**

Table 5.3 shows that two 500 L reactor tanks will be used for the dissolution and combining of transparent gel and GO. The first 500 L reactor tank will be used to prepare transparent gel, which will then be stored in the -20 C refrigerator. The second 500 L reactor tank will be used to mix transparent gel with GO before extruding the ACGO gel into ACGO beads. Three 300 L reactor tanks hold 40 and 65%wt H_2SO_4 and GO. In the ACGO bead fabrication stage, an extrusion basin is used to obtain ACGO beads, and a dialysis basin is used for the dialysis process for pH adjustment. Four pumps are used to feed 40 and 65%wt H_2SO_4 and GO into separate 500 L reactor tanks, as well as to extrude ACGO gel into ACGO beads. Table 5.4 depicts the equipment characteristics.

Table 5.4 Characteristic of equipment [78]

No.	Equipment	Picture
1	500 L reactor tank	
2	300 L reactor tank	
3	-20 °C refrigerator	
4	Extrusion basin	
5	Dialysis basin	

Table. 5.4 Characteristic of equipment (continued) [78]

No.	Equipment	Picture
6	Collected basin	
7	Pump	

Conclusion

The scaling-up of ACGO bead fabrication is divided into two scales: pilot scale and near commercial scale. The pilot scale provides 510 L of ACGO gel, while the commercial scale holds 2,550 L of ACGO gel. The pilot scale and commercial scale plant models are designed using the fabrication protocol of the ACGO bead fabrication in laboratory scale. The related equipment and size of the reactor tanks are chosen with the total amount of raw material usage as a priority.

Chapter 6
Commercialization plan

One of the most difficult aspects of becoming an entrepreneur is commercializing a new product, thus the owner needs to be both physically and emotionally ready for it. Many of these business owners hope that their businesses will succeed as well. However, from an academic standpoint, managerial expertise helps explain how those great entrepreneurs succeeded. As a result, the marketing strategy for the ACGO beads will be illustrated in this chapter. The commercialization plan is implemented focusing on important topics which are market analysis, PEST analysis, SWOT analysis, STP analysis, the marketing (4Ps), operation plan, financial plan, challenge and opportunity, intellectual property and brand and brand management.

6.1 Market analysis

6.1.1 Trend and growth

Nanocelluloses are naturally abundant materials that are promising as an emerging "green material" because they are biocompatible, biodegradable, and renewable [1, 45]. They were applicable to be a dominant component in various industries such as food packaging [79], a pickering emulsifier [80-82], film [47, 63, 83-87], water purification [24, 68, 88-90], energy [91-96], security paper [97, 98], healthcare [99-101], and so on. The aforementioned nanocellulose applications had a direct impact on nanocellulose market demand, which was projected to be 783 M USD in 2025 [102]. The ACGO bead is one of these nanocellulose-based materials that is suitable for water purification because it is a water-insoluble material and ideal water adsorbent. [25, 43, 55, 66, 103, 104]. ACGO aerogel can be used to adsorb methylene blue (MB) [105], malachite green (MG) [103], organic dyes [106], and antibiotics [27, 43]. Therefore, ACGO beads have the potential to adsorb water contaminants. According to Thai fishery department (2022), shrimp is the highest aquatic animal export of Thailand approximately 158,295 tons (49,850 mln THB in 2021) and 44,584 tons (15,053 mln THB in 2022). This number of exports declined during the Covid-19 pandemic. The value of shrimp exports exceeded that of squid,

which ranks second with 10,858 mln THB in 2021 and 4,337 mln THB in 2022. The export value of shrimp and squid was 5:1. Furthermore, fish was the third aquatic animal export. As a result, the shrimp market offers an excellent opportunity to promote ACGO beads as an alternative product in the shrimp farming industry.

Following the identification of the target market, the researcher developed a survey to ask shrimp farmers in Chachoengsao and Nakhornsrithammarat which chemicals have an impact on shrimp farming. According to the findings, farmers concluded that nitrite, ammonia, and nitrate were the top three most damaging chemicals to their farms, which is consistent with previous reports. Previous studies have shown that ammonia and nitrite buildup in shrimp farms would disrupt excretion and metabolism, reducing shrimp growth and survival rates [107-109]. Furthermore, nitrite was formed from ammonia through nitrification [110].

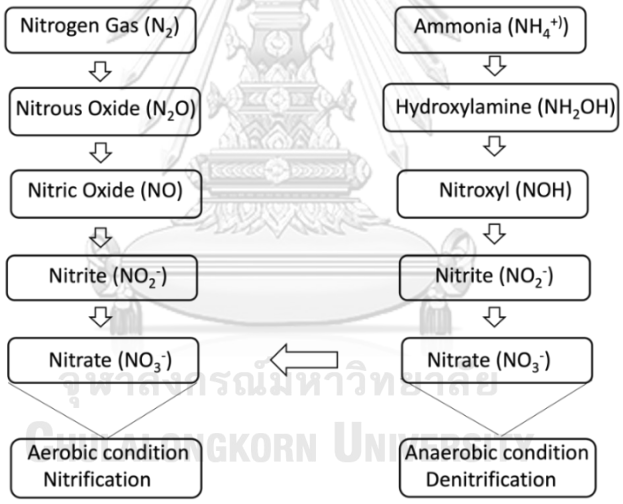


Figure 6.1 Reaction of nitrification and denitrification [111]

The literature review yielded the same results as the primary surveys from 373 shrimp farmers, as shown in the market survey (6.1.2). According to survey results, the top three chemicals affecting their farms were ammonia, nitrite, and nitrate, in that order.

6.1.2 Competitive landscape and market size

The competitive landscape is critical in developing a competitive strategy. The newcomer must conduct research to determine who the market's major players

are, what products they offer, and how high the quality of those products is. The information would assist the newcomer in mitigating risks as they entered the market.

6.1.2.1 Competitor

Currently, the activated carbon is the most materials used in water treatment market due to its cost competitiveness. Other adsorbents consist of activated charcoal, ion exchange resin, ceramic, graphite, graphene, graphene oxide, cellulose nanocrystal (CNC), cellulose nanofibers (CNFs), RO membrane and Chlorine, in which among adsorbents graphene owns the highest price but high adsorption efficiency.

Table 6.1 Cost of adsorbent [78]

No.	Adsorbent per 1 kg	Cost (THB/kg)	Cost (US $/kg)
1	Activated carbon	30	1
2	Activated charcoal	22	0.73
3	Ion exchange resin	21	0.7
4	Ceramic	42	1.4
5	Graphite	30	1
6	Graphene	3,300	110
7	Graphene oxide	900	30
8	Cellulose nanocrystal (CNC)	120	4
9	Cellulose nanofibers (CNFs)	99	3.3
10	RO membrane	120 per piece	-
11	Chlorine	35	1.16
12	**Proposed ACGO beads**	**113**	**3.71**

Note: 1 US $ = 30 Baht [112]

From Table 6.1, The ACGO bead costs 113 THB per kg while activated carbon costs 30 THB per kg or The ACGO bead cost is higher than the activated carbon about 4 times. The two main reasons that the cost of the ACGO bead is high because GO cost is still high even using only small amount and the H_2SO_4 used in the dissolution process is still high as shown in Table 6.2.

6.1.2.2 Market size

According to the cost of ACGO beads is much higher comparing to other existing adsorbents. It is difficult for agricultures changing existing adsorbents to be ACGO beads. Therefore, the researcher would like to provide shrimp farming market size and other potential alternative market sizes to be optional for the ACGO beads for potential markets. Therefore, the chosen markets consist of shrimp farming and drinking water purification markets.

According to the Thai Fishery Department (2022) [113], shrimp is Thailand's most important aquatic animal export, with 158,295 tons (49,850 M THB in 2021) and 44,584 tons (15,053 M THB in 2022). The decrease in export value in 2022 was due to the Covid-19 scenario. Shrimp export value was substantially higher than squid export value, which was 10,858 M Baht in 2021 and 4,337 M THB in 2022. The export value of shrimp and squid was almost 5:1. Furthermore, fish was the third aquatic animal export.

Table 6.2 Statistic of Thai shrimp and squid export between 2021-2022 [114]

Year	Export product	Amount (ton)	Value (mln THB)
2021	Shrimp	158,295	49,850
	Squid		10,858
2022	Shrimp	44,584	15,053
	Squid		4,337

ตารางที่ 4 จำนวนฟาร์มเลี้ยงกุ้งทะเลในจังหวัดที่สำคัญ จำแนกตามประเภทการเลี้ยง ปี 2564

จังหวัด	ประเภทการเลี้ยง					
	รวม		กึ่งพัฒนา		พัฒนา	
	จำนวนฟาร์ม	%	จำนวนฟาร์ม	%	จำนวนฟาร์ม	%
รวม	***26,263***	***100.00***	***2,819***	***100.00***	***23,444***	***100.00***
ฉะเชิงเทรา	3,574	13.61	-	-	3,574	15.25
นครศรีธรรมราช	1,970	7.50	-	-	1,970	8.40
สมุทรปราการ	1,964	7.48	1,136	40.30	828	3.53
จังหวัดอื่น ๆ	18,755	71.41	1,683	59.70	17,072	72.82

Figure 6.2 Statistic of Thai shrimp farm in 2021 [114]

6.1.3 Market survey

After studying the trend and growth, the result shows that the target market is expanding, so the complementation equipment in the shrimp business should also expand in conjunction with the growth of the shrimp farming market. Because the target market of ACGO beads will be the water treatment business of shrimp farming, the market survey questions on this topic will be specific to the water treatment system of their farms. The questionnaires contain nine questions, including the age of the shrimp farmers, farm location, experience, existing water treatment cost, opinion on cost reduction, opinion on the new water treatment system, the proportion of shrimp farming, chemicals affecting water quality, and existing water treatment methodology. The researcher gathered 373 responses from shrimp farmers. The survey results are shown below.

Question no. 1: The age of the shrimp farmers

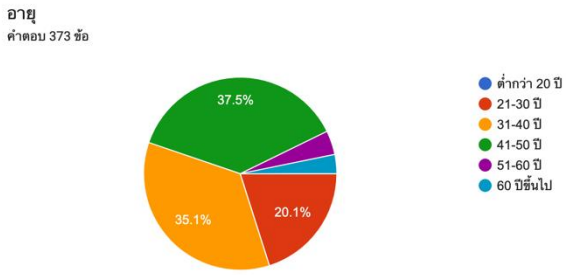


Figure 6.3 Age of the shrimp farmers

The results show that the majority of shrimp farmers are 41-50 years old (37.5%), 31-40 years old (35.1%), 21-30 years old (20.0%), and 51-60 years old, more than 60 years old as descending.

Question no. 2: Farm location

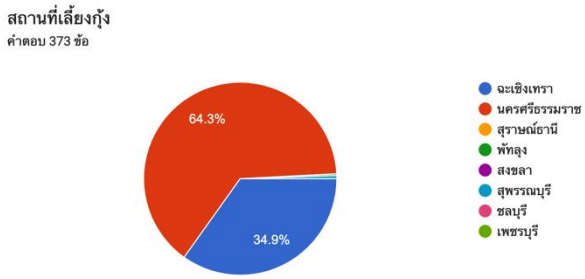


Figure 6.4 Location of farm

The researcher selected three farm locations for the market survey: Nakhonsrithammarat (64.3%), Chachoengsao (34.9%), and Suphanburi (the rest).

Question no. 3: Experience

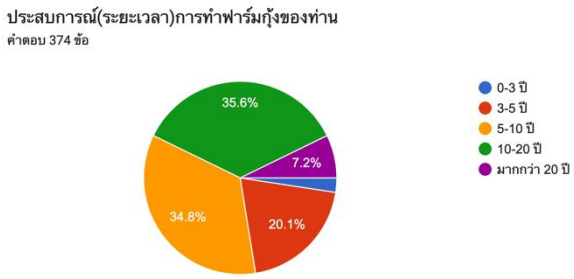


Figure 6.5 Experience of shrimp farming

Most farmers gain experience between the ages of 10 and 20 (35.6%), with those aged 5 to 10 and over 20 gaining the least.

Question no. 4: Existing cost for water treatment

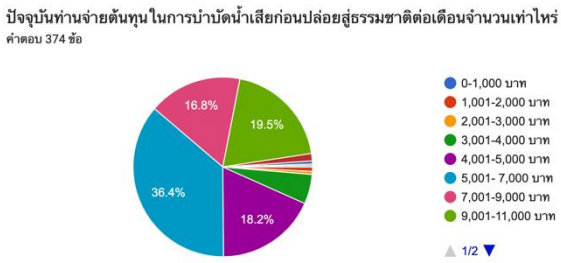


Figure 6.6 Existing cost of water treatment

The majority of shrimp farmers spend between 5,001 and 7,000 THB per month (36.4%), 9,001 and 11,000 THB per month (19.45%), and 7,001 and 9,000 THB per month (16.80%), respectively.

Question no. 5: Opinion on the cost decreasing

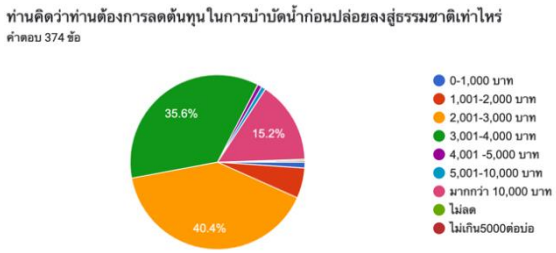


Figure 6.7 How much cost that shrimp farmers prefer to decrease

This question seeks to determine how much cost most farmers would prefer to reduce. The results show that most farmers would like to save 2,001 - 3000 THB per month (40.4%), 3,001 - 4000 THB per month (35.6%), indicating that the expected monthly water treatment cost is around 3,001 - 4,000 THB.

Question no. 6: Opinion on the new water treatment system

Figure 6.8 Opinion on the new water treatment system

This is an important question to ask if a new water treatment product has been introduced to shrimp farmers. What will pique their interest in the new product? The survey clearly shows that most farmers (61.8%) are interested if the price is lower than the existing products by 15-30% and also provides better efficiency.

Question no. 7: Proportion of shrimp farming

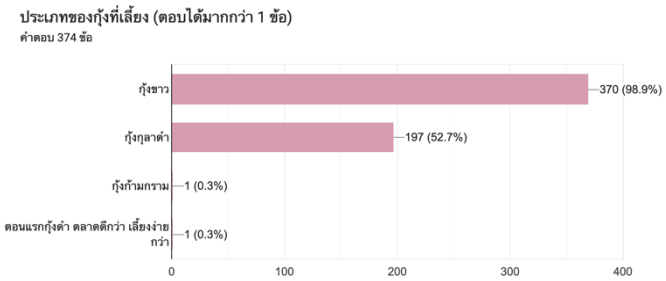


Figure 6.9 Proportion of shrimp species

The three most common types of shrimp for commercialization are white shrimp (the majority), tiger prawns, and lobster. Therefore, most contaminants emitted by white shrimp are being studied first.

Question no. 8: Chemicals impacted to water quality

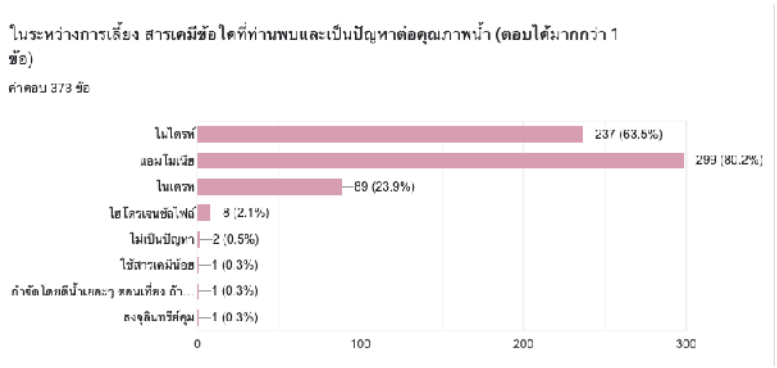


Figure 6.10 Chemicals impacted to water quality

According to survey results, ammonia is the most significant chemical influencing water quality in shrimp farms, followed by nitrite and nitrate.

Question no. 9: Existing methodology of water treatment

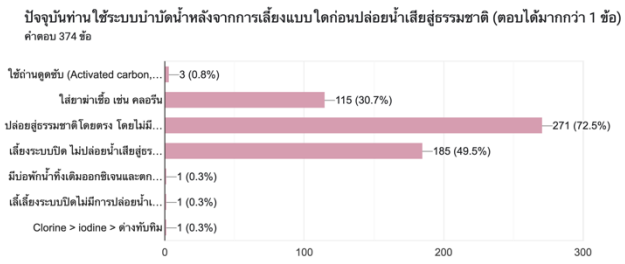


Figure 6.11 Existing methodology of water treatment

Most shrimp farmers use the method of directly emitting water from the shrimp farm to the surrounding environment, with no water treatment process. According to the survey results, contaminants in shrimp farming may be toxic to natural systems.

6.2 PEST analysis

PEST analysis is a business tool for understanding the big picture impact or macro factor level. PEST composition consists of four factors: political (P), economic (E), social (S), and technological (T).

6.2.1 Political (P)

Figure 6.12 Sustainable development goals (SDGs) [115]

As part of the "Do not leave anyone behind" concept, the United Nations (UN) organization established sustainable development goals (SDGs) to assist the world in addressing current issues. The goals are to address poverty, inequality, global warming, and peace. The SDGs included 17 goals, including no poverty (1), zero hunger (2), good health and well-being (3), quality education (4), gender equality (5), clean water and sanitation (6), affordable and clean energy (7), decent work and economic growth (8), industry, innovation, and infrastructure (9), reduce inequalities (10), sustainable cities and communities (11), responsible consumption and production (12), climate action (13), life below water (14), life on land (15), and peace, justice and strong institutions (16), and partnership for the goals (17). The ACGO bead, being a green material, adheres to SDG 6, 7, 9, and 14.

6.2.2 Economic (E)

Cellulose's diverse applications drive future demand for the cellulose market, which is expected to be worth USD 783 million by 2025 [102]. AC was utilized as film [47], aerogel [61], and pellet [116] while ACGO composites were applicable in products such as adsorbent [27, 105], film [47], and bead [103]. It

suggests that ACGO composites could be used in industries such as film and water treatment.

6.2.3 Social (S)

AC and ACGO beads are eco-friendly since they are biodegradable, biocompatible, and renewable. In comparison to prior reports on ionic liquids [117], NaOH/urea [71, 118], and phosphoric acid [65] the production procedure is not difficult, time-consuming, or energy-consuming. The benefits of the proposed fabrication methodology will be evident during the manufacturing and scaling-up processes, resulting in cost management and waste reduction.

6.2.4 Technology (T)

The existing technology to manufacture AC and ACGO beads is complicated and inefficient. The researcher successfully developed a simple and cost-effective technology for fabricating AC and ACGO beads in this study. The new technology has the potential to outperform existing technologies in many ways, including process simplicity, solvent usage, and time consumption.

6.3 SWOT Analysis

The internal and external factors on ACGO beads must be considered prior to the SWOT analysis. Internal factors influencing ACGO beads, which are related to ACGO bead fabrication methodology, are raw materials, stability, and budgeting, while external factors are customer perspectives and marketing. SWOT analysis considers both internal and external factors. The following is a SWOT analysis of AC and ACGO beads.

6.3.1 Strengths

The AC and ACGO beads demonstrate significant strengths in terms of increasing the percentage of opportunity to be a competitive product, as shown below:

1) The fabrication methodology is simpler, less time, and energy-consuming than existing methodologies, so it has a cost advantage, but it requires intellectual property protection to protect the copyright.

2) The raw material (eucalyptus paper) is abundant and inexpensive.

3) The GO preparation is not complicated.

4) The adsorption efficiency is high.

6.3.2 Weakness

The weakness of AC and ACGO beads are shown as following.

1) AC and ACGO beads have a low strength when compared to plastic beads. The high pressure of the water flow rate could break the AC and ACGO beads.

2) The beads must be immersed in water at all times; otherwise, the water inside the beads will evaporate, affecting the bead size and physical properties.

6.3.3 Opportunity

AC and ACGO beads are used not only for contaminant adsorption in shrimp farms, but also in other industries such as film, cosmetics, and concrete. Furthermore, the product's high adsorption efficiency may be applicable to a high-value market. The opportunities will primarily be discussed in light of the PESTEL analysis, which includes topics such as political (P), economic (E), social (S), technology (T), environment (E), and legal (L).

1) According to the economic (E) and technological (T), the AC and ACGO beads can be used as an alternative adsorbent for dyes, antibiotics, microplastics, VOC compounds, and heavy metals.

2) In accordance with the technology (T), the AC and ACGO composites could be formed into film, microspheres, aerogel, and monolith.

3) The AC and ACGO composites could be used in other industries such as drinking water cartridges, energy storage, corrosion resistant and biochemical devices that are in accordance with the economic (E), technology (T), environment (E), legal (L), and social (S).

6.3.4 Threat

The following threats may be significant factors in making AC and ACGO beads unsustainable in the long run, and the treatments will be discussed primarily in light of PESTEL analysis, such as opportunities.

1) Product costs may have an impact on long-term business. According to the combination of AC and GO, the AC raw-material price is stable, but the GO price fluctuates in response to economic (E), technological (T), environmental (E), legal (L), and social (S) factors.

2) The bead fabrication process will be easily duplicated due to the simplicity of the method, which may affect the price competitiveness in which technology (T) is used.

6.4 STP (Segmentation, Targeting and Positioning) Analysis

Targeting the right group of customers would reduce marketing costs while increasing customer efficiency. The STP strategy is an important tool for precisely reaching target customer groups. The STP strategy intends to use this for shrimp farms.

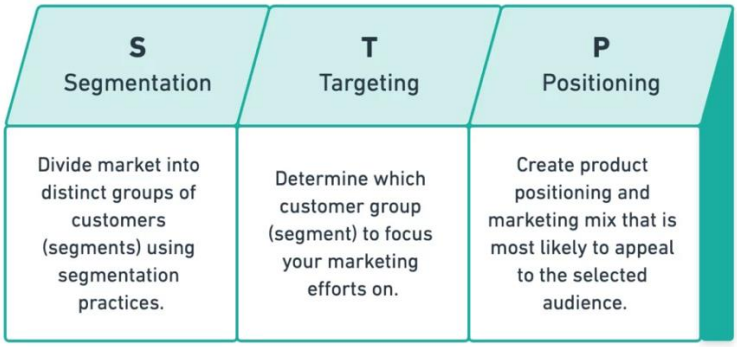


Figure 6.13 STP marketing model [119]

6.4.1 Segmentation

S (segmentation): The shrimp farmers are classified into four groups: those who spend $9,001-11,000 per month (73), those who spend $5,001-9,000 per month (199), those who use chlorine for water treatment (115), and those who directly emit water to the environment (271).

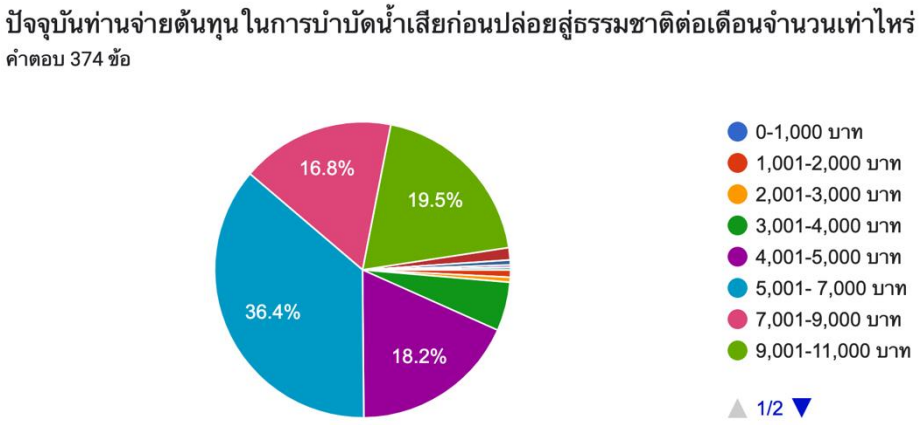


Figure 6.14 Responses from farmers about cost of water treatment

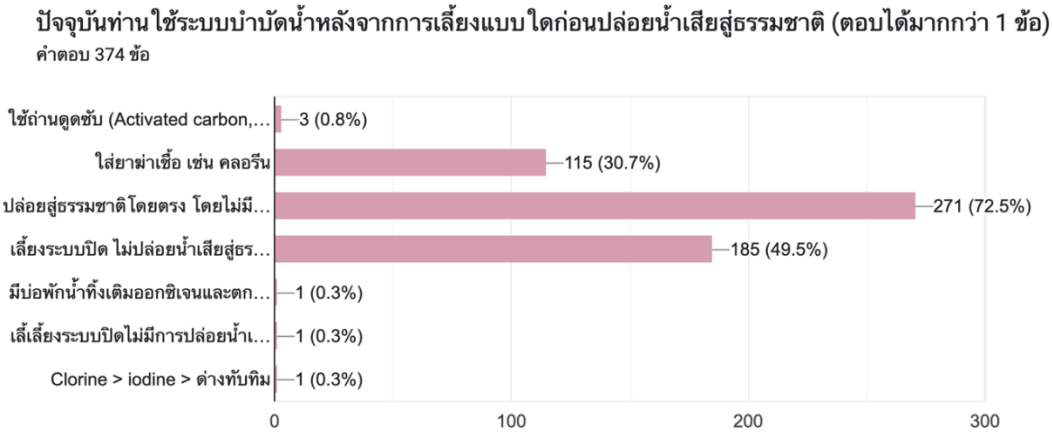


Figure 6.15 Responses from farmers about water treatment methodology

6.4.2 Targeting

The group most likely to be targeted is the group that directly emits water into the natural environment and supports the use of alternative green water treatment materials, even if they are more expensive. This group does not have a water treatment technique that could harm the environment. Furthermore, replacing old water would be expensive as compared to treating water with the current treatment method. The ACGO beads may have a good possibility to fill the gap in water treatment in this group. Furthermore, the ACGO beads will be supplied to shrimp producers for free testing.

6.4.3 Positioning

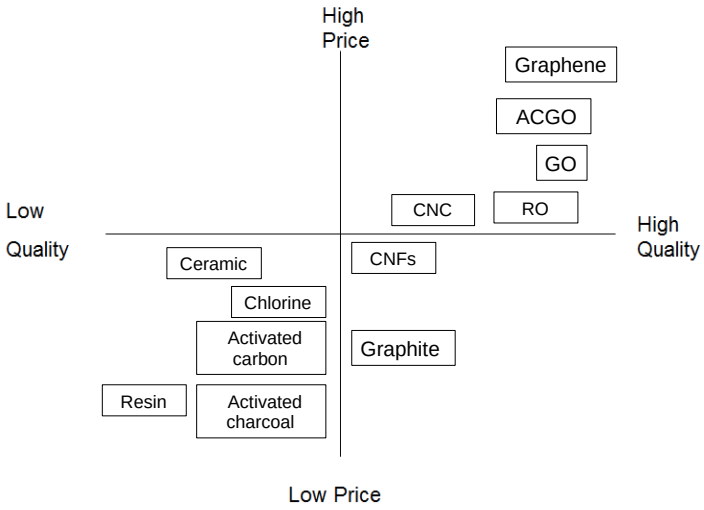


Figure 6.16 Positioning of ACGO beads comparing to existing products

ACGO beads are positioned in the high-price and high-quality section, while RO is positioned in the medium-price and high-quality section, and activated carbon is positioned in the low-price and medium-quality section. The initial investment for new product development (NPD) is obviously high, resulting in a high cost. However, in the long run, production costs will be lower, and ACGO prices may be competitive. Furthermore, the low cost and high adsorption ability of ACGO beads suggests that they may be appropriate in high-end markets such as premium water treatment for drinking, high-value fish farming, or household businesses, which could be studied further for commercialization.

6.5 The marketing (4Ps)

The four factors that must be thoroughly examined in order to create an effective market plan were identified. Product, price, promotion, and location are among the factors. The 4P proposal would be advantageous in terms of getting the product directly to the right customers.

6.5.1 Product

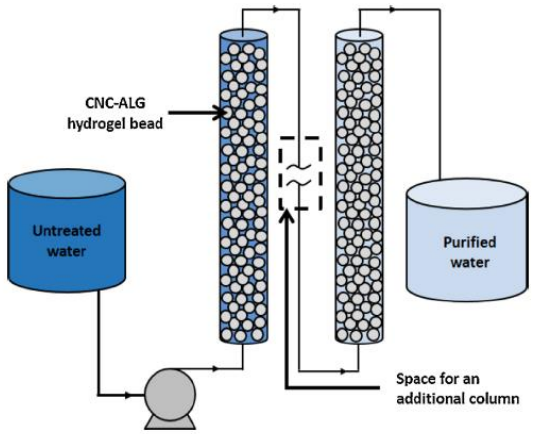
The product is an ACGO bead, and the product is determined by eight significant factors, including satisfying needs, a unique selling point, a feature,

quality, branding, packaging, warranties, and services [120]. To begin, the ACGO could meet the needs of shrimp farmers by eliminating ammonia, nitrite, and nitrate, all of which are caused by poor water quality. Shrimp will die because of poor water quality, as will shrimp diseases. Second, the environmentally friendly material is a distinct selling point. The ACGO beads are made of amorphous cellulose and GO, with amorphous cellulose promising to be a green material (biocompatible, biodegradable, and renewable) [121, 122]. Moreover, the very low amount of GO dispersion in ACGO beads (1 g eucalyptus: 0.5 ml GO) is considered to be a very low proportion when compared to the amount of existing adsorbents used, such as activated carbon, activated charcoal, ceramic, and resin.

Third, the feature of ACGO is the bead. The surface area of beads is greater than that of fiber, aerogel, and monolith. The greater the surface area, the greater the possibility of surface area contacting between adsorbate and adsorbent. Fourth, the adsorption quality of ACGO composites is higher than that of activated carbon, biochar, and activated charcoal, as shown in Table 2.2 from previous studies. Fifth, because the cost of scaling-up production is still high, the researcher has not created a new brand for ACGO beads yet. It will take time to improve the production protocol in order to have competitive production. As a result, in the first stage, the products will be distributed as trial products for use in shrimp farms, and assessment data will be collected. Sixth, the packaging will be designed as a column, as shown in Figure 6.18 and sold per column. Because the high flow rate of water could break the beads into fragments, the column packaging will help absorb water pressure without breaking the beads. Furthermore, fragments flowing into the column will be protected. Finally, warranty and after-sales services will be provided. The products can be recycled at least five times so that customers do not need to purchase a new one after the first use. On-site recycling will be provided by the company. After 5 cycles, a customer could buy a new product and sell the old ones back to the company.

To design packaging, two topics must be considered: shrimp farm characteristics and how to determine whether the designed packaging is feasible for the shrimp farm. Other factors to consider include the product's natural behavior and

maintenance strategy. The column as shown in Figure 6.17, appropriate for packaging of shrimp farming business.



Scheme 1. Schematic diagram of a fixed bed adsorption column process employing CNC-ALG hydrogel beads as dye adsorbents.

Figure 6.17 Example of beads in column [88]

6.5.2 Price

The cost of ACGO beads is 113 THB/kg, which is approximately four times the cost of activated carbon, and when all other costs are considered, the total cost is 160 THB/kg. Topic 6.2 goes into greater detail.

Shrimp farming business overview

In order to set the reasonable price of ACGO beads, all perspectives require to be considered such as water standard in shrimp farm, life cycle of shrimp, activities in shrimp farming, sizes of shrimp farm and shrimp farm management system.

Table 6.3 Water standard in shrimp farm [123, 124]

No.	Quality index	Unit	Standard	Measurement method
1	pH	-	6.5-9.0	Colorimetric, pH papers, Nesslerization
2	Biochemical Oxygen Demand (BOD)	mg/L	< 20	Winkler titration, Polarographic, Electrometric
3	Suspended Solids	mg N/L	< 70	
4	NH_3-N	mg P/L	< 1.1	Cadmium reduction

				method
5	Total Phosphorus	mg/L	< 0.4	
6	H_2S	mg/L	< 0.01	
7	Total Nitrogen	mg N/L	< 4.0	Phenate method

According to the results of the survey, NH_3-N and total nitrogen are listed as water quality factors in Table 6.3. According to previous research, the ACGO composite can adsorb not only nitrogen but also phosphorus and H_2S.

Sizes of shrimp farm

There are three types of shrimp farming systems in Thai shrimp aquaculture: extensive, semi-intensive, and intensive. Capital, equipment, labor, skill, land, water, seed (post-larvae), feed, and energy are used to categorize each system. Table 6.4 summarizes the various shrimp farming systems [109].

Table 6.4 Shrimp farm management system types [109]

Management aspects	**Extensive system**	**Semi-intensive system**	**Intensive system***
Feed types	Natural	Natural and supplemental	Formulated high protein
Water management	Tidal	Tidal and pumping	Pumping and aeration
Pond sizes (ha)	2 to 20	1 to 5	0.1 to 1.0
Stocking rates (post-larvae/m^2)	0.1 to 1	1 to 5	6 to greater than 25
Production (kg/ha year)	More than 500	500 to 5,000	5,000 to 20,000

In an intensive farming system, most farms have a size of around 6.25 rai and a total water amount of around 12,000,000 liters, as shown in Table 6.6. The amount of water will be used to calculate the amount of ACGO beads used in the farms.

Table 6.5 Overview information of the intensive shrimp farming system [109]

Management aspects	Intensive system*
Feed types	Formulated high protein
Water management	Pumping and aeration
Pond sizes (ha), Note: Width: 25 m, Length: 400 m	0.1 to 1.0
Min width = 25 – 50 m, 1 rai = 1600 m^2, 1 ache = 6.25 m^2	
Water level = 1-1.2 m	
Pond sizes (rai)	6.25 rai
Pond sizes (m^2)	10,000 m^2
Estimated total water amount (m^3)	12,000 m^3 /12,000,000 L
Stocking rates (post-larvae/m^2)	6 to greater than 25
Estimated total stock rates	60,000 to 250,000
Production (kg/ha year)	5,000 to 20,000

The proportion of activated carbon to water used for water treatment is 480 cc (480 g) to 280 L [125]. It takes approximately 1 kg of activated carbon to treat 560 L of water in a shrimp farm. Consequently, one shrimp farm (12,000,000 L of water) requires approximately 21,428 kg or 21 tons of activated carbon, which costs approximately 642,840 THB (21,480 × 30 from Table 6.1). Assuming that the ACGO beads require 21,428 kg to treat the same amount of water, the cost will be approximately THB 3,857,040 (21,480 × 180), or 6 times that of activated carbon. However, the ACGO beads can be used repeatedly because they can be reused via recycling process. Qiufang Yao [27] demonstrated in an antibiotic adsorption study that the cellulose-GO composite retained 78.9% adsorption efficiency after reusing and recycling 10 times. In contrast to activated carbon, which cannot be reused. As a result, replacing new activated carbon for ten times-shrimp farming will cost approximately 6,428,400 THB, whereas using ACGO beads with ten-time recyclability will cost approximately 3,857,040 THB, which is less than 1.67 times. Therefore, the long-term cost of ACGO bead is competitive compared to activated carbon cost.

Shrimp life cycle

Intensive system is the most famous for Thai shrimp farming and the overview process of one shrimp crop is shown as Figure 6.18 and detail of activities are shown in Table 6.6.

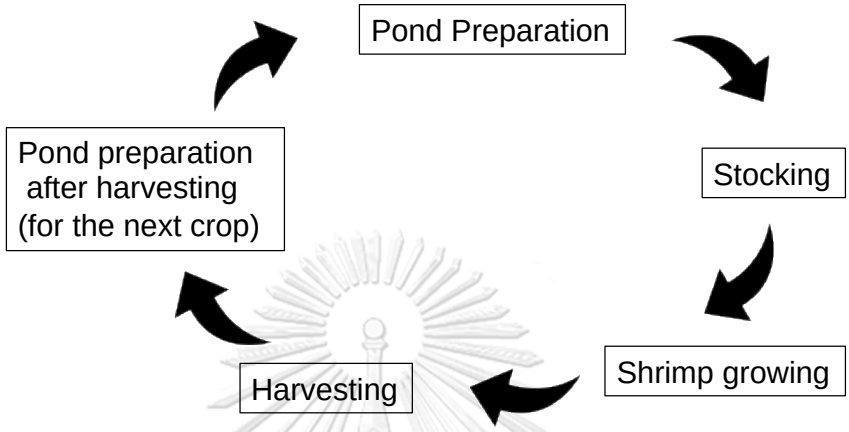


Figure 6.18 One-Crop cycle of Intensive system [109]

One crop of shrimp life cycle consists of pond preparation, stocking, shrimp growing, harvesting, preparation after harvesting.

Table 6.6 Activities in one-crop cycle of intensive system [126]

No.	Activity	Detail	Day
1	Pond preparation	1. 1-1.2 meters deep, chorine: disinfectants, Limestone and burnt lime to adjust pH; 7.5-8.5 2. Fertiliser : promote the growth of algae as a natural food for shrimps "water-colour developing"; colour from the colour of plankton developed in the pond	1 - 7
2	Stocking	1. post-larvae up to stage 15 (15 days of age after hatching) 2. Post-larvae are accommodated in acclimatization tanks or nurser ponds to adjust to pond conditions, particularly to salinity and temperature levels before being stocked (How much for each size of pond)	7 - 10

Table 6.6 Activities in one-crop cycle of intensive system [126] (continued)

No.	Activity	Detail	Day
3	Shrimp growing	1. wide variety of chemicals and antibiotics are used for promoting growth, maintaining water quality and preventing diseases 2. Exchange of water is applied for preserving the water quality, and oxygenation systems are used to maintain a sufficient oxygen level in the ponds 3. Growing the shrimps to a market size take about 120 days or more	10 - 130
4	Harvesting	1. Capturing from the outflowing water, the rest harvested by nets or picked up by hand 2. Shrimps put into icy water asap 3. Sorted by sized and transported to the market or directly to the planys	130 - 135
5	Pond preparation after harvesting (for the next crop)	Removed sediment, sun drying, remove sludge	135 - 145

According to Table 6.6, overall activities for one crop shrimp farming include pond preparation, stocking, shrimp growing, harvesting, and pond preparation after harvesting, each of which requires a different type of water treatment for its specific purpose. For example, during the shrimp growing stage, ACGO beads are required to maintain water quality for shrimp growth, whereas during the harvesting stage, ACGO beads are required for water treatment.

6.5.3 Place

ACGO beads are a new absorbent on the market with a high cost of fabrication when compared to existing adsorbents such as activated carbon, activated charcoal, resin, and ceramic. To save money, direct sales to customers and online media channels will be prioritized.

Direct sales: The researcher will approach shrimp farmers, mostly in Chachengsao and Nakhonsri Thammarat, to pitch ACGO beads. In the first three months, 100 farmers are expected to be targeted, and the team will consist of two people.

Online: The first online source created to promote the ACGO beads is Facebook. Facebook is a free and widely accessible online resource. The Facebook online advertisement will also be shared on the Instagram, Twitter, and Line applications. Furthermore, the ACGO beads will be available on shoppee.com in the adsorbent module with two administrators.

6.5.4 Promotion

The ACGO beads are considered to be a technological push. To be clear, there is a demand for adsorbents to maintain water quality, but shrimp farmers do not want to increase their costs, so they continue to use activated carbon, activated charcoal, resin, and ceramic as adsorbents because those products are less expensive. However, existing adsorbents are being questioned as to whether they are environmentally friendly materials. The ACGO beads are considered to be the most efficient adsorbent promising biodegradability, renewability, and biocompatibility, but the price is still prohibitively expensive for farmers.

As a result, the researcher would like to offer two promotions. To begin, we have a free trial usage experience for one crop of shrimp farming. The free usage promotion will provide customers with firsthand knowledge of the efficiency of ACGO beads in comparison to other adsorbents. Second, if the farmer decides to purchase ACGO beads for one farm, the researcher will provide free ACGO beads for another farm. In exchange, farmers must provide experience data to researchers for product assessment and development to benefit from the provided promotion.

6.6 Operational plan

The operation plan is a critical tool for a company during the execution phase. According to [127], general questions that the entrepreneur should ask before developing the operation plan include what goals must be achieved, who is responsible for those goals, when those goals must be completed, and how much the

cost will be. Furthermore, there are five steps to creating a successful operation business plan, including strategic business planning, focusing on the most important goals, using leading indicators rather than lagging indicators, defining appropriate KPIs, and creating a clear communication channel. The first step in developing an operation plan is to develop a strategic business plan. The strategic plan is divided into four topics based on the initial concept: goals, responsibility, milestones, and cost budgeting.

The objectives must be met in three sections: front-end, back-end office successfully set up, and revenue generation. The front-end office is made up of the departments of marketing and service, while the back-end office is made up of the departments of finance and accounting. The ACGO business front-end office places a premium on marketing and customer service.

6.6.1 Staffs

A start-up company composes department of accounting, marketing, production and service. Two staffs will be employed in accounting department. Accounting department is responsible for backend section. The accounting team is responsible of recording the company's inflow and outflow and managing all related documents. Marketing department is responsible for marketing and customer relationship. The marketing team consists of ten people who are responsible both online and offline marketing. The marketing team must visit farms, demonstrate tutorials, and add customers to Facebook and the data center. The staffs of production consist of five people responsible for ACGO production and machine operation. The service or maintenance team consists of three people who are responsible for product maintenance. All employees' salaries are assumed to be 20,000 THB/person/month. The staff planning is shown in Table 6.7.

Table 6.7 Departments of a company

No.	Department	Amount of employee (people)	Responsibility
1	Accounting	2	Documentation
2	Marketing	10	Marketing
3	Production	5	Manufacturing
4	Service	3	After service

6.6.2 Tools and equipment

The tools and equipment are described in chapter 5.

6.6.3 Marketing

Face-to-face marketing has several advantages over online marketing, including a more positive customer experience, effective communication, better understanding, and trust [128]. Marketing will initially target shrimp farmers in Chachoengsao because this is the location with the most shrimp farming in Thailand and is close to Bangkok. According to [129], there were ten marketing strategies to increase sales revenue, including using social media, creating video tutorials, blogging, using search engine optimization (SEO), hiring influencers, having a significant lead magnet, using Facebook advertisements, using LinkedIn, creating an affiliate program, and using email marketing sequences. Because the initial stage of marketing will be onsite or face-to-face marketing focusing on direct communication, the tutorials and Facebook will be shown to the right customers in Chachoengsao, the first two marketing strategies to be implemented by ACGO are creating video tutorials and creating Facebook advertisements.

6.7 Financial plan

The financial plan of ACGO beads were simulated into three scenarios which are base, best and worst scenarios. The key factor to categorize each scenario is sell quantity in which entrepreneur can simulate in various constrains to search for risk and opportunity. For financial plan simulation, each scenario consists of six parts which are initial investment, annual sale revenue, expense, operating income, cashflow and analysis of investment return.

6.7.1 Base case scenario

6.7.1.1 Initial investment

According to Table 6.8, the initial investment consists of initial equipment, labor installation, factory construction and office equipment.

Table 6.8 Initial investment structure

No.	Initial investment list	Price (THB/unit)	Quantity (Unit)	Total (THB)
1	Initial equipment	-	-	-
	1.1 500 L reactor tank	53,000	4 (tank)	212,000
	1.2 300 L reactor tank	30,000	5 (tank)	150,000
	1.3 -20°C refrigerator	57,000	2 (unit)	114,000
	1.4 Extrusion basin	800	10 (basin)	8,000
	1.5 Dialysis basin	800	10 (basin)	8,000
	1.6 Collected basin	800	10 (basin)	8,000
	1.7 Pump	1,000	100 (pump)	100,000
	1.8 Office equipment	430,000	1 (unit)	430,000
			Total initial equipment	**1,030,000**
2	Factory construction	20,000	100 (m^2)	2,000,000
			Total initial investment	**3,030,000**

According to Table 6.8, all initial equipment and factory construction lifetime are assumed to be 5 years and the salvage value of both assets are zero.

Depreciation [130] = (Asset cost – Salvage value) / Lifetime of asset

Depreciation of initial equipment = (1,030,000 – 0)/5 = 206,000 THB/year

Depreciation of factory construction = (2,000,000 – 0)/10 = 200,000 THB/year

Total depreciation = 406,000 THB/year

6.7.1.2 Annual sale revenue

Table 6.9 Annual sale revenue

Year	2023	2024	2025	2026	2027
Amount of farm (farm, 9.5% growth)	525	575	629	689	755
ACGO bead quantity per farm (kg)	300	300	300	300	300
Selling price/kg (THB, 9.5% growth)	200	210	221	232	243
Total revenue (THB)	**31,500,000**	**36,217,125**	**41,640,639**	**47,876,325**	**55,045,805**

According to Table 6.9, the assumption factors for annual sale revenue are shown as following.

- The company can sell ACGO beads to 525 shrimp farms (2% of total Thai shrimp farms as shown in Table 6.12) in 2023 and each farm uses 300 kg of ACGO bead per year.
- The selling price per kg of ACGO beads is 200 THB/kg at year 2023 and the selling price has been increased 9.5% every year.
- Growth of amount of farm is 9.5% per year regarding to the average growth of adsorbent business.

6.7.1.3 Expense

Table 6.10 Expense

No.	Expense	Payment rate	Unit	Expense Year 2022 (Year 0)	Expense growth (% per year)
1	**Cost of sale**				
1.1	Material	140	THB/kg	-	9.5%
1.2	Employee	20,000	THB/person/month (20 employee)	-	-
1.3	Utilities	50,000	THB/month	-	9.5%
2.1	Land rental	20,000	THB/month	240,000	-
1.4	DP of initial equipment	206,000	THB/year	-	-
1.5	DP of factory construction	200,000	THB/year		
2	**Sell and administration cost**				
2.1	Admin salary	30,000	THB/person/month (2 admins)		
2.2	Sale commission	3%	3% of annual revenue	-	-
2.3	Logistics	10%	10% of annual revenue	-	-
3	**Corporate tax**	**20%**	**20% of operating income**	-	-

The assumption factors for expense of the base case are shown as Table 6.10. The material cost starts at 140 THB/kg at year 2023 and the material cost has been increased 9.5% per year. The main cost structure for manufacturing ACGO beads includes eucalyptus paper, chemicals in the dissolution process, GO, and other costs. Other costs include manpower, facility, and other unknowns. The cost calculation methodology is shown in Table 6.11 and assumes that 1 kg of eucalyptus paper is used as the initial material for the cost calculation simulation.

Table 6.11 Cost estimation to fabricate ACGO beads using 1 kg of eucalyptus paper as raw material

Type of cost	Calculation method	Price (THB/kg)
Eucalyptus paper	-	50
Dissolution process	Usage amount of H_2SO_4 to dissolve 1 g eucalyptus paper (8 mL) × Price of 97 %wt H_2SO_4 per 1 kg × Proportion of 55 %wt to 97 %wt H_2SO_4 × 1,000 (1 kg of eucalyptus paper)	498
GO	1 g eucalyptus paper: 0.5 mL GO	450
Other costs	10%	115
	Total cost	**1,113**

As shown in Table 6.11, 1 kg of eucalyptus paper requires 1,113 THB to be transformed into ACGO beads, and the beads weigh approximately 9.5 kg or ~10 kg (1 kg of eucalyptus paper + 8 kg of H_2SO_4 + 0.5 kg of GO). As a result, the cost/kg of ACGO beads is 1,113/10 = 113 THB/kg (approximately four times that of activated carbon). With other additional cost, the material cost is approximately estimated to be 140 THB/kg. In addition, the cost of 140 THB/kg already includes recycle cost.

Because existing adsorbents in the market have an average lifetime period of about 6 months per cycle, a repeatable usage period of 6 months per cycle is assumed. According to the [27], the recycle process's chemicals and equipment are made up of 5%wt NaOH solution. The cost of NaOH per Liter is 70 THB; if 1 L can recycle 500 kg of ACGO bead, then 15,000 kg of ACGO bead will use NaOH approximately 30 L or 2,100 THB; however, this value is not significant enough to be a representative number, so the researcher decides to assume the recycle cost is already included in the material cost. According to [27], the cellulose-GO composite retained 78.9% adsorption efficiency after 10 times of reuse and recycling, a 3.9% decrease from the initial usage. because the ACGO beads can be reused but the activated carbon material must be renewed every six months. As a result, the long-term cost of ACGO beads will be competitive with activated carbon.

- The cost to hire an employee is 20,000 THB/person/month.

- The utility cost is 50,000 THB/month and has been increased 9.5% per year.
- The total depreciation rate is from depreciation of initial equipment and factory construction.
- The land rental cost is 20,000 THB/month.
- The sale commission is assumed to be 3% of annual revenue.
- The logistic cost is assumed to be 10% of annual revenue.
- The tax is assumed to be 20% of operating income as of corporate tax.

6.7.1.4 Operating income

Table 6.12 Operating Income

Year	2023 (THB)	2024 (THB)	2025 (THB)	2026 (THB)	2027 (THB)
Total revenue	31,500,000	37,769,288	45,286,320	54,299,430	65,106,374
Cost of sale					
Material	22,050,000	26,438,501	31,700,424	38,009,601	45,574,462
Employee	4,800,000	4,800,000	4,800,000	4,800,000	4,800,000
Utilities	600,000	657,000	719,415	787,759	862,597
Land rental	240,000	240,000	240,000	240,000	240,000
DP of initial equipment	206,000	206,000	206,000	206,000	206,000
DP of factory construction	200,000	200,000	200,000	200,000	200,000
Total cost of sale	**28,096,000**	**32,541,501**	**37,865,839**	**44,243,360**	**51,883,058**
Sell & administration cost					
Admin salary	720,000	720,000	720,000	720,000	720,000
Sale commission	945,000	1,133,079	1,358,590	1,628,983	1,953,191
Logistics	3,150,000	3,776,929	4,528,632	5,429,943	6,510,637
Total sell & administration cost	**4,815,000**	**5,630,007**	**6,607,222**	**7,778,926**	**9,183,829**
Total expense	**32,911,000**	**38,171,509**	**44,473,061**	**52,022,286**	**61,066,887**
Operating income	**(1,411,000)**	**(402,221)**	**813,259**	**2,277,144**	**4,039,487**
Tax (20%)	0	0	162,652	455,429	807,897
Net profit	**(1,411,000)**	**(402,221)**	**650,608**	**1,821,715**	**3,231,590**

According to Table 6.12, operating income of year 2023 and 2024 becomes negative and the tax is negative in these two years. The net profit starts to be positive between year 2025 to 2027.

6.7.1.5 Cashflow

Table 6.13 Cashflow

Year	2022 (THB)	2023 (THB)	2024 (THB)	2025 (THB)	2026 (THB)	2027 (THB)
Cashflow from operation						
Net profit	0	(1,128,800)	(321,777)	650,608	1,821,715	3,231,590
DP of initial equipment	0	206,000	206,000	206,000	206,000	206,000
DP of factory construction	0	200,000	200,000	200,000	200,000	200,000
Total	**0**	**(1,005,000)**	**3,779**	**1,056,608**	**2,227,715**	**3,637,590**
Cashflow from investment						
Total initial investment	(3,030,000)	-	-	-	-	-
Net cashflow	(3,030,000)	(1,005,000)	3,779	1,056,608	2,227,715	3,637,590
PV factor (Discount rate 14%)	1	0.88	0.77	0.67	0.59	0.52
Present value	**(3,030,000)**	**(881,579)**	**2,908**	**713,180**	**1,318,986**	**1,889,250**

According to Table 6.13, the discount rate calculation is shown as following.

Discount rate = Risk-Free rate + Beta adjusted equity risk premium + Size premium + Specific company risk premium [131].

The assumption of each component is shown as following.

1. Risk-free rate: the assumption uses the 20-year treasury bond yield of 3.87 [132].
2. Equity risk premium: between 4.0% and 7.0%. The equity risk premium representative is 4, used in calculation.
3. Beta: 1
4. Size premium: between 3.0% and 5.0%, The size premium representative is 3, used in calculation

5. Specific company risk premium: 3.13% assumed to be investor's expected return.

Therefore, the equity discount rate is 14% (3.87 + 4 + 3 + 3.13).

According to [131], if the discount rate is greater than 25%, the company is undervalued. As a result, the study's discount rate is 14%, indicating that it is reasonable to be a representative value. Furthermore, the company is small because a large company should have a lower discount rate than 14%. Therefore, the representative for discount rate is 14%.

The present value of year 2022 and 2023 are negative because the year 2022 is year zero so that the initial investment is calculated in this year. The year 2023 becomes negative because of sale volume and depreciation deduction. The present value starts to be positive from year 2024 to 2027.

6.7.1.6 Analysis of investment return

Table 6.14 Analysis of investment return

Scenario	NPV (THB)	IRR (%)	Payback period (Year)
Base case	12,745	14%	4.25

According to Table 6.14, the NPV is positive showing that the business is feasible. The IRR (14%) is higher than the discount rate (14%) implies that the business is valuable. However, the payback period is 4.25 years.

6.7.2 Worst case scenario

6.7.2.1 Initial investment

The initial investment of the worst-case scenario is the same as the base case and the best-case scenario, as shown in Table 6.8.

6.7.2.2 Annual sale revenue

Table 6.15 Annual sale revenue

Year	2023	2024	2025	2026	2027
Amount of farm (farm, 9.5% growth)	480	526	576	630	690
ACGO bead quantity per farm (kg)	300	300	300	300	300
Selling price/kg (THB, 9.5% growth)	200	219	240	263	288
Total revenue (THB)	**28,800,000**	**34,531,920**	**41,404,635**	**49,645,193**	**59,525,827**

According to Table 6.15, the assumption factors for annual sale revenue are shown as following.

- The company can sell ACGO beads to 480 shrimp farms in 2023 and each farm uses 300 kg of ACGO bead per year.
- The selling price per kg of ACGO beads is 200 THB/kg at year 2023 and the selling price has been increased 9.5% every year.
- Growth of amount of farm is 9.5% per year regarding to the average growth of adsorbent business.

6.7.2.3 Expense

The expense of the worst-case scenario is the same as the base case and the best-case scenario, as shown in Table 6.10.

6.7.2.4 Operating income

Table 6.16 Operating Income

Year	2023 (THB)	2024 (THB)	2025 (THB)	2026 (THB)	2027 (THB)
Total revenue	**28,800,000**	**34,531,920**	**41,404,635**	**49,645,193**	**59,525,827**
Cost of sale					
Material	20,160,000	24,172,344	28,983,245	34,751,635	41,668,079
Employee	4,800,000	4,800,000	4,800,000	4,800,000	4,800,000
Utilities	600,000	657,000	719,415	787,759	862,597
Land rental	240,000	240,000	240,000	240,000	240,000
DP of initial equipment	206,000	206,000	206,000	206,000	206,000
DP of factory construction	200,000	200,000	200,000	200,000	200,000
Total cost of sale	**26,206,000**	**30,275,344**	**35,148,660**	**40,985,394**	**47,976,676**
Sell and administration cost					
Admin salary	720,000	720,000	720,000	720,000	720,000
Sale commission	864,000	1,035,958	1,242,139	1,489,356	1,785,775
Logistics	2,880,000	3,453,192	4,140,464	4,964,519	5,952,583
Total sell & administration cost	**4,464,000**	**5,209,150**	**6,102,603**	**7,173,875**	**8,458,358**
Total expense	**30,670,000**	**35,484,494**	**41,251,262**	**48,159,270**	**56,435,033**
Operating income	**(1,870,000)**	**(952,574)**	**153,373**	**1,485,923**	**3,090,794**
Tax (20%)	0	0	30,675	297,185	618,159
Net profit	**(1,870,000)**	**(952,574)**	**122,698**	**1,188,739**	**2,472,635**

According to Table 6.16, operating income of year 2023 and 2024 becomes negative and corporate tax is negative in these two years. The net profit starts to be positive between year 2025 to 2027.

6.7.2.5 Cashflow

Table 6.17 Cashflow

Year	Year 0 (THB)	2023 (THB)	2024 (THB)	2025 (THB)	2026 (THB)	2027 (THB)
Cashflow from operation						
Net profit	0	(1,870,000)	(952,574)	122,698	1,188,739	2,472,635
DP of initial equipment	0	206,000	206,000	206,000	206,000	206,000
DP of factory construction	0	200,000	200,000	200,000	200,000	200,000
Cashflow from investment						
Total initial investment	(3,030,000)	-	-	-	-	-
Net cashflow	**(3,030,000)**	**(1,464,000)**	**(546,574)**	**528,698**	**1,594,739**	**2,878,635**
PV factor	1	0.88	0.77	0.67	0.59	0.52
Present value	**(3,030,000)**	**(1,284,211)**	**(420,571)**	**356,856**	**944,213**	**1,495,073**

The present value of the year 2022 and 2023 are negative because the year 2022 is year zero so that the initial investment is calculated in this year. The year 2023 becomes negative because of sale volume and depreciation. The present value starts to be positive from year 2024 to 2027.

6.7.2.6 Analysis of investment return

Table 6.18 Analysis of investment return

Scenario	NPV (THB)	IRR (%)	Payback period (Year)
Worst case	(1,938,639)	0%	5.1

According to Table 6.18, the NPV is negative showing that the business is not feasible. The IRR (0%) is lower than the discount rate (14%) implies that the business is not valuable. However, the payback period is 5 years still feasible for the project timeline.

6.7.3 Best case scenario

6.7.3.1 Initial investment

The initial investment of the best-case scenario is the same as the base case and the worst-case scenario, as shown in Table 6.8.

6.7.3.2 Annual sale revenue

Table 6.19 Annual sale revenue

Year	2023	2024	2025	2026	2027
Amount of farm (farms, 9.5% growth)	550	602	659	722	791
ACGO bead quantity per farm (kg)	300	300	300	300	300
Selling price/kg (THB, 9.5% growth)	200	219	240	263	288
Total revenue (THB)	**33,000,000**	**39,567,825**	**47,442,811**	**6,885,117**	**68,206,677**

According to Table 6.19, the assumption factors for annual sale revenue are shown as following.

- Year 2022 is assumed to be year zero, in which the sale revenue is zero.
- The company can sell ACGO beads to 550 shrimp farms in 2023 and each farm uses 300 kg of ACGO bead per year.
- The selling price per kg of ACGO beads is 200 THB/kg at year 2023 and the selling price has been increased 9.5% every year.
- Growth of amount of farm is 9.5% per year regarding to the average growth of adsorbent business.

6.7.3.3 Expense

The expense of the worst-case scenario is the same as the base case and the worst-case scenario, as shown in Table 6.10

6.7.3.4 Operating income

Table 6.20 Operating Income

Year	2023 (THB)	2024 (THB)	2025 (THB)	2026 (THB)	2027 (THB)
Total revenue	**33,000,000**	**39,567,825**	**47,442,811**	**56,885,117**	**68,206,677**
Cost of sale					
Material	23,100,000	27,697,478	33,209,968	39,819,582	47,744,674
Employee	4,800,000	4,800,000	4,800,000	4,800,000	4,800,000
Utilities	600,000	657,000	719,415	787,759	862,597
Land rental	240,000	240,000	240,000	240,000	240,000
DP of initial equipment	206,000	206,000	206,000	206,000	206,000
DP of factory construction	200,000	200,000	200,000	200,000	200,000
Total cost of sale	**29,146,000**	**33,800,478**	**39,375,383**	**46,053,341**	**54,053,271**
Sell & administration cost					
Admin salary	720,000	720,000	720,000	720,000	720,000
Sale commission	990,000	1,187,035	1,423,284	1,706,554	2,046,200
Logistics	3,300,000	3,956,783	4,744,281	5,688,512	6,820,668
Total sell & administration cost	**5,010,000**	**5,863,817**	**6,887,565**	**8,115,065**	**9,586,868**
Total expense	**34,156,000**	**39,664,295**	**46,262,948**	**54,168,406**	**63,640,139**
Operating income	(1,156,000)	(96,470)	1,179,863	2,716,710	4,566,539
Tax (20%)	0	0	235,973	543,342	913,308
Net profit	**(1,156,000)**	**(96,470)**	**943,890**	**2,173,368**	**3,653,231**

According to Table 6.20, operating income of year 2023 becomes negative and corporate tax is negative in this year. The net profit starts to be positive from year 2024 to 2027.

6.7.3.5 Cashflow

Table 6.21 Cashflow

Year	2022 (THB)	2023 (THB)	2024 (THB)	2025 (THB)	2026 (THB)	2027 (THB)
Cashflow from operation						
Net profit	0	(1,156,000)	(96,470)	943,890	2,173,368	3,653,231
DP of initial equipment	0	206,000	206,000	206,000	206,000	206,000
DP of factory construction	0	200,000	200,000	200,000	200,000	200,000
Total	**0**	**(750,000)**	**309,530**	**1,349,890**	**2,579,368**	**4,059,231**
Cashflow from investment						
Total initial investment	(3,030,000)	-	-	-	-	-
Net cashflow	(3,030,000)	(750,000)	309,530	1,349,890	2,579,368	4,059,231
PV factor	1	0.88	0.77	0.67	0.59	0.52
Present value	**(3,030,000)**	**(657,895)**	**238,173**	**911,138**	**1,527,193**	**2,108,237**

According to Table 6.21, the present value of year 2022 is negative because the year 2022 is year zero so that the initial investment is calculated in this year. The present value starts to be positive from year 2023 to 2027.

6.7.3.6 Analysis of investment return

Table 6.22 Analysis of investment return

Scenario	NPV (THB)	IRR (%)	Payback period (Year)
Best case	1,096,847	22%	3.85

According to Table 6.22, the NPV is positive showing that the business is feasible. The IRR (22%) is much higher than the discount rate (14%) implies that the business is high valuable. In addition, the payback period is 3.85 years attractively to be invested.

6.7.4 Analysis of investment return for different scenarios

Table 6.23 Analysis of investment return for different scenarios

Scenario	NPV (THB)	IRR (%)	Payback period (Year)
Best case	1,096,847	22%	3.85
Base case	12,745	14%	4.25
Worst case	(1,938,639)	0%	5.10

The positive NPVs of the base and best-case scenarios show that the ACGO business is feasible. The IRR of both scenarios are higher than discount rate also guarantee that the business is valuable. However, the base case has longer payback period than the best case but both payback period of best and base case scenarios is still feasible. The worst-case scenario provides negative NPV and IRR, showing that the if the business is in the worst case, the company requires to consider about exit strategies.

6.7.5 Sensitivity analysis

Three factors used for sensitivity analysis are sale volume, selling price and material cost. All factors will be studied by correlation between the factor and IRR.

Table 6.24 Correlation between sale volume and IRR

Scenario	Sale volume (Farms/year)	IRR
Best	550	22%
Base	525	14%
Worst	480	0%

According to Table 6.24, the sale volume is roughly equivalent to the quantity of shrimp farms. The data shows that the higher product volume can be sold to customers, the higher IRR will be obtained. Therefore, the sale volume must not below than 480 farms then the IRR will be positive. This assumption has controllable factors which are sale price (200 THB/kg) and material price (140 THB/kg).

Table 6.25 Correlation between sale price and IRR

Scenario	Sale price (THB/kg)	IRR
Best	210	53%
Base	200	16%
Worst	190	-30%

According to Table 6.25, the controllable factors are sale volume (525 farms/year) and material price (140 THB/kg). The data shows correlation between the sale volume and IRR, the optimize sale price should be set around 200 THB/kg to have positive IRR and higher than discount rate (14%).

Table 6.26 Correlation between material cost and IRR

Scenario	Material cost (THB/kg)	IRR
Best	130	58%
Base	140	16%
Worst	150	-40%

According to Table 6.26, the controllable factors are sale volume (525 farms/year) and sale price (200 THB/kg). The data show that with the sale volume and IRR, the optimize material cost should be around 140 THB/kg to have positive IRR and higher discount rate (14%).

In conclusion, the first three significant factors of financial projection are sale volume, sale price and material cost. Both the base and best-case scenarios show that the financial measurement factors are feasible, making it a good candidate for investors. In contrast, the worst-case scenarios show that the financial measurement factors are not feasible under those assumptions, but the IRR is still positive. Annual sale volume, sale price, discount rate, material costs, and selling price are all important factors that have a direct impact on financial projections. As a result, the financial projection can be improved by adjusting those important factors.

6.8 Challenge and opportunity

The cost and marketing competitiveness of ACGO beads pose a significant challenge. In the short term, the researcher would face high production costs due to the prices of GO and H_2SO_4. Furthermore, the scaling-up process is not yet complete. However, the cost of materials is expected to fall in the future, resulting in greater cost competitiveness. However, the advantage of the ACGO beads is high-efficiency adsorption compared to existing adsorbents, which causes the researcher to be concerned only with production cost improvement rather than efficiency improvement. Furthermore, if the production cost is successfully reduced, the mass volume of ACGO beads or other forms could be applied in a variety of industries.

6.9 Intellectual property

The contribution of ACGO beads is not about the product, but about the cellulose dissolution process. To the best of our knowledge, no one has reported using two different concentrations of H_2SO_4 for cellulose dissolution. When compared to previous reports, this new methodology uses less H_2SO_4 and takes less time to dissolve. These two advantages are considered to be the main contribution of this work.

The researcher decided to register the new cellulose dissolution methodology for Petty patent for two reasons.

1. This is an improvement to the cellulose dissolution process, but it is not considered advanced technology.
2. The enhancement could provide additional benefits in terms of usage.

The right of petty patent is provided in the registration for petty patent. The petty patent is valid for 6 years from the date of registration and can be extended twice (2 years each time for a total of 10 years).

The IP protection protocol must protect against copyright infringement. Secret keeping, documentation, trademark, registration, and investment are all part of the protection protocols. To begin, the entrepreneur must keep the key secret of their work undisclosed or may disclose it to others if a nondisclosure agreement has been signed. Second, the entrepreneurs must keep original evidence. Evidence can include

experimental data, blueprints, drawings, records, and related plans that demonstrate originality. The date and signature are two of the most important pieces of evidence because they are critical points in an investigation. ACGO bead evidence includes experiment data, sulfuric acid usage, and technical equipment. Third, trademark registration should be a top priority. The name and logo of the new product must be meticulously designed because a good name and logo will be a significant advantage over existing companies in the same industry. Fourth, the entrepreneur must not only keep confidential information secret, but also register with the government section in order to obtain official evidence. The key documents that the entrepreneur should prioritize are intellectual property and company secrets. Finally, IP is a company's asset. The entrepreneur can make an investment in intellectual property by charging a fee to those who benefit from the IP. Table 6.16 contains a summary of IP protection protocols.

Table 6.27 IP protection protocols [133]

No.	Detail	Description
1	Secret keeping	Require a nondisclosure agreement
2	Documentation	Keep evidence of original
3	Trademark	Trademark registration
4	Registration	IP
5	Investment	IP fee charging

6.10 Brand and brand management

When customers want to buy a product, they normally consider which brands to purchase. If customers continue to purchase the same product, this is considered customer brand recognition. According to [126], a brand is defined as "the tangible elements that are attached to the product to differentiate the product from the competition" or "a symbol that distinguishes one product from others." More than just a regular brand, if a brand is recognized by the majority of people, it assists the entrepreneur in meeting yearly or quarterly revenue targets. Starbucks, McDonald's, KFC, GUCCI, Hermes, Chanel, Saint Laurent, Balenciaga, and Celine are examples

of well-known brands in the beverage, food, and clothing markets that the majority of customers recognize.

Special brands (individual or private brands), family brands, collective brands (group brands), and national brands are the four types of brands [134]. ACGO bead's branding strategy will be classified as a special brand because it is in the process of developing a trademark. A trademark, according to [126], is the specific name of a good or service that distinguishes one product from another. As illustrated in Figure 6.22, a brand or trademark plays an important role for a consumer or a business.

Table 6.28 Role of brands to consumers and business [134]

Consumers	Businesses
- Identify the origin of products - Assume responsibility for the manufacturer or distributor - Reduce search costs - Commitment to business - Tools icon - Signs of quality - Reduce the risk of product purchase and consumption decisions	- Identification means to simplify product description or differentiation - Means of legal learning to protect the unique characteristics of the product - Means provide products with unique associations - Signs of quality level for consumers - Source of competitive advantage - Source of financial return

Source: Own development

According to Table 6.26, a brand has an impact on consumers and businesses from two perspectives: consumer and business, and it also has a direct impact on a company's yearly sales revenue. Customers are influenced by brands in a variety of ways, including product recognition, creditability, cost management, business promise, and quality guarantee. The entrepreneur of the ACGO bead product must then prioritize the brand design issue in accordance with the lessons learned from previous reports, resulting in a reduced risk of brand strategy.

At the same time, the entrepreneur must learn about a brand from the perspectives of business management, such as product differentiation, legal learning, quality assurance, competitiveness, and finance. Customers recognize a brand from various angles. Customers, for example, recognize Chanel as a luxury and expensive brand. As a result, one of the most important factors to prioritize is branding strategy. The entrepreneur will learn about regulation and documentation from a legal standpoint. The back-end system of a company is another important key success factor because many documents must be generated and signed by the authority prior to the execution process.

Customers believe that a good brand will guarantee them quality. For example, some customers believe that if they purchase a product from the PRADA brand, the

seller will provide them with premium benefits over other brands, such as premium product materials, warranty, and after-sales services, and so on. Customers in a business unit realize the positioning of a business unit's product from the standpoint of competitiveness. Customers recognize, for example, that PRADA products, which are among the most expensive bags and clothes in the world, will provide superior quality than other brands in the industry, which is why customers are willing to pay for a product. Brand management is another critical topic on which an entrepreneur should focus because, in order to increase the percentage of a successful brand, an entrepreneur must be concerned with issues such as brand building, brand positioning, brand protection, brand promotion, brand value exploitation, and so on [134].

Finally, branding strategy is one of the most important tools for entrepreneurs to increase the percentage of company success. A good or bad brand will be recognized theoretically in two ways: consumer recognition and business recognition. Furthermore, to build a successful brand, the entrepreneur must understand brand management. A good branding strategy also includes good brand design and management.

Chapter 7
Conclusions and recommendations

7.1 Conclusions & Discussions

Four phases in this dissertation are studies to answer research objectives. The four phases consist of studying existing ACGO hybrid structure fabrication to develop process of AC and ACGO bead fabrication, developing product prototype and characterization, developing scaling-up production plan and commercialization plan implementation.

7.1.1 The result of Phase I: Developing process of AC and ACGO bead fabrication

In this research, we developed an efficient method for the fabrication of amorphous cellulose-graphene oxide bead. AC and ACGO beads were successfully manufactured in two steps of dissolution and regeneration. The dissolution process employed two different concentrations of sulfuric acid under varying conditions, with DI water serving as the precipitating agent. The obtained AC and ACGO beads were white and light brown in color, respectively.

According to a practical and economic standpoint, the proposed methodology was a lean methodology. In practice, the sulfuric aqueous solution system had advantages over other solvent systems such as direct dissolution of high molecular weight cellulose, low amount usage, and an easy cleaning process when compared to other solvent systems that could not dissolve high molecular weight cellulose and required a lot of energy to dissolve. When compared to other systems, the sulfuric solvent system was the most practical and cost-effective. As a result, the proposed process is advantageous for future large-scale production of AC and ACGO composites, particularly in the field of water adsorption.

7.1.2 The result of Phase II: Developing product prototype and characterization

Uniform AC and ACGO beads were successfully developed, as well as small AC and ACGO quasi-sphere beads. Scientific techniques were used to characterize amorphous cellulose (AC) and amorphous cellulose-graphene oxide (ACGO) beads.

Scanning electron microscopy (SEM), fourier-transform infrared (FTIR), and raman spectroscopies (Raman) were used to confirm the entrapment of graphene oxide (GO) by amorphous cellulose. The average diameter of AC and ACGO beads was 2.11 ± 0.13 mm and 2.14 ± 0.12 mm, respectively. Molecular, thermal, and structural characterization techniques were used to investigate the structural change of semicrystalline eucalyptus fiber after gelatinization and subsequent regeneration. The transformation of cellulose I to cellulose II was confirmed by FTIR spectra and XRD patterns. The presence of GO within amorphous cellulose chains in ACGO beads was confirmed by Raman spectra. Because of the added GO, the SEM images revealed a smoother surface of ACGO beads compared to AC. Characterization techniques confirm the success of ACGO bead fabrication, but the beads must still be calibrated by a standard calibration company or government section to be considered a legal product.

7.1.3 The result of Phase III: Developing scaling-up production plan

The scaling-up plan is divided into pilot and near-commercialization scales, with the production quantity of ACGO gel per day serving as the criterion for categorization. The pilot and near commercialization scale ACGO gel quantities per day are 510 L and 2,550 L, respectively. The pilot scale requires 1,875 extrusion syringes and 8 hours of work time to reach the minimum production quantity per day, while the near commercialization scale requires 9,375 extrusion syringes and 8 hours of work time.

One of the critical issues is the scaling-up plan process. The scaling-up process is designed in accordance with laboratory scale process methodology, and it is divided into three stages: ACGO gel preparation, ACGO bead fabrication, and packaging. The model has been adjusted to achieve a minimum production quantity

per day of the pilot and a scale close to commercialization. The plant model is then created. Due to the size of the investment and the limitations of the fabrication protocol, the plant model is designed for semi-continuous production. The initial equipment usage is directly related to the investment strategy of starting small before expanding. The scaling-up plan of the pilot and near commercialization scale is the initiate idea to generate more efficient automation production factory. In addition, the plans can be customized to feasible for other scaling-up products.

7.1.4 The result of Phase IV: Commercialization plan implementation

The commercialization plan is examined from multiple perspectives in order to assess business feasibility. The ACGO composites market trend has been increasing, and ACGO composites can be used in a variety of industries, indicating that the future market is promising. ACGO beads' target market is water treatment for Thai shrimp farming because they have the potential to adsorb nitrite, which is one of the contaminants in a shrimp farm. Internal and external analysis models are used in business analysis. The product is competitive against activated carbon due to the unique properties of the ACGO bead, which are biocompatible, biodegradable, renewable, and reusable. According to the financial projection, if the financing is in the worst-case scenario, the company must prepare to execute exit strategies. During the launching stage, the brand management and operation plan are used. The commercialization plan contributes to the entrepreneur's initial idea in the field of new product development and can be tailored to a specific startup.

7.2 Recommendations for future research

ACGO beads could be made more cost-effective and simpler by improving the fabrication protocol. The composite could include other materials besides graphene oxide, such as activated carbon, to be more cost-effective. In addition to their high adsorption efficiency, ACGO beads could be used in other high-level markets. One of the alternative markets for ACGO beads is shrimp farming. However, there are other markets where the ACGO beads could be used as adsorbents, such as fish farming, hospital wastewater management, water suppliers, and drinking water.

7.3 Limitations

The techniques were successful in characterizing the ACGOs beads, but the adsorption experiment was not completed due to the Covid-19 pandemic. However, the effectiveness of ACGOs in comparison to other existing materials was demonstrated in a previous report.

Appendixs

Noted: Preparation of different chemical concentration

Preparing 40 v/v% H_2SO_4 and 65 v/v% H_2SO_4

The formula used is $C_1V_1 = C_2V_2$

C_1: Concentration of 97% H_2SO_4

C_2: Concentration of expected% H_2SO_4

V_1: Volume of 97% H_2SO_4

V_2: Volume of expected% H_2SO_4

For example1. The researcher would like to prepare 40 %v/v H_2SO_4, 400 mL.

$C_1V_1 = C_2V_2$

$97\% \times A = 40\% \times 400$, $A = 165$

So that the researcher must prepare 165 mL of 97% H_2SO_4 and 235 mL of water (400-165)

C_1: 97%

C_2: 65%

V_1: A

V_2: 400

For example2. The researcher would like to prepare 65 %v/v H_2SO_4, 400 mL.

$C_1V_1 = C_2V_2$

$97\% \times A = 65\% \times 400$, $A = 268$

So that the researcher must prepare 268 mL of 97% H_2SO_4 and 132 mL of water (400-268)

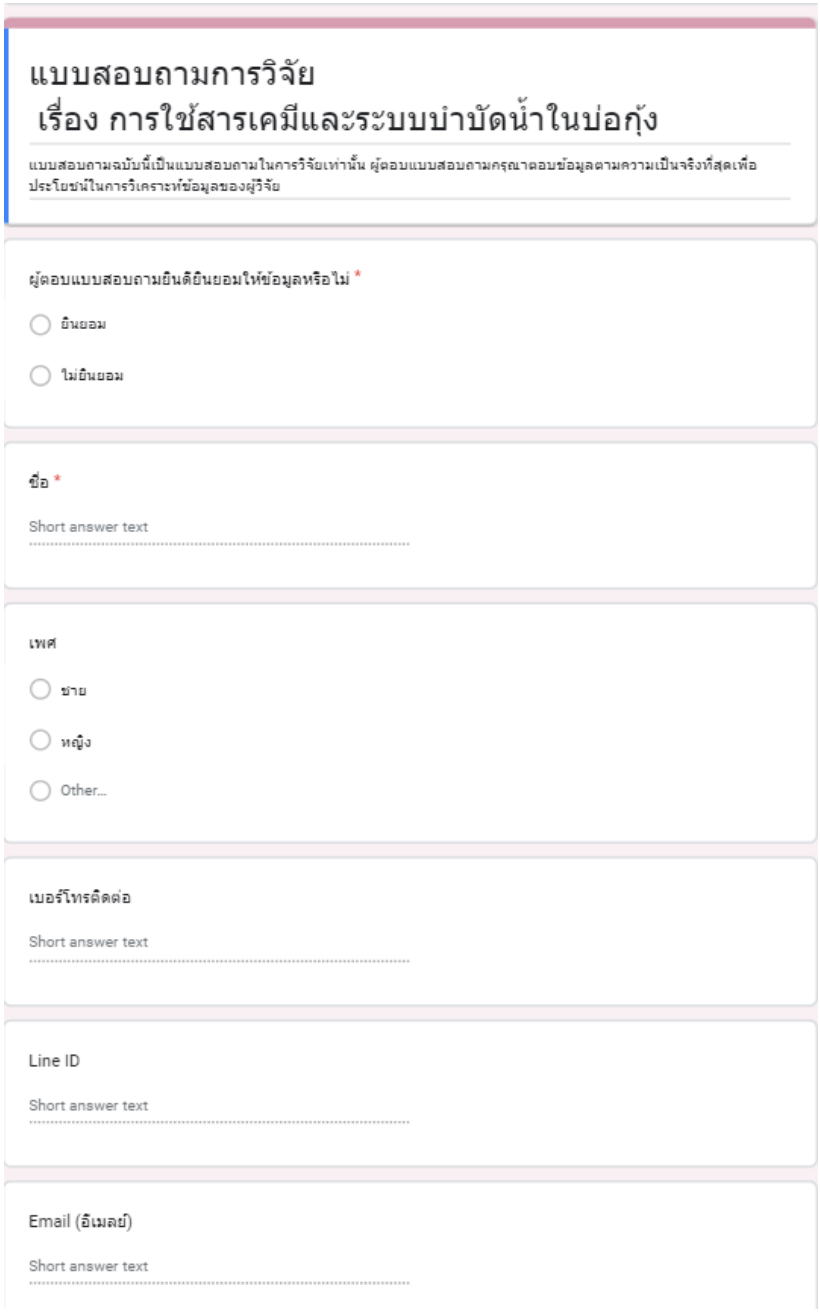
C_1: 97%

C_2: 70%

V_1: A

V_2: 400

Questionnaire



แบบสอบถามการวิจัย
เรื่อง การใช้สารเคมีและระบบบำบัดน้ำในบ่อกุ้ง

แบบสอบถามฉบับนี้เป็นแบบสอบถามในการวิจัยเท่านั้น ผู้ตอบแบบสอบถามกรุณาตอบข้อมูลตามความเป็นจริงที่สุดเพื่อประโยชน์ในการวิเคราะห์ข้อมูลของผู้วิจัย

ผู้ตอบแบบสอบถามยินดียินยอมให้ข้อมูลหรือไม่ *

- ยินยอม
- ไม่ยินยอม

ชื่อ *

Short answer text

เพศ

- ชาย
- หญิง
- Other...

เบอร์โทรติดต่อ

Short answer text

Line ID

Short answer text

Email (อีเมลย์)

Short answer text

อายุ *

- ต่ำกว่า 20 ปี
- 21-30 ปี
- 31-40 ปี
- 41-50 ปี
- 51-60 ปี
- 60 ปีขึ้นไป

สถานที่เลี้ยงกุ้ง *

- ฉะเชิงเทรา
- นครศรีธรรมราช
- สุราษฎ์ธานี
- พัทลุง
- สงขลา
- สุพรรณบุรี
- ชลบุรี
- เพชรบุรี
- Other...

ประสบการณ์(ระยะเวลา)การทำฟาร์มกุ้งของท่าน *

- 0-3 ปี
- 3-5 ปี
- 5-10 ปี
- 10-20 ปี
- มากกว่า 20 ปี

ประเภทของกุ้งที่เลี้ยง (ตอบได้มากกว่า 1 ข้อ) *

- [ ] กุ้งขาว
- [ ] กุ้งกุลาดำ
- [ ] กุ้งก้ามกราม
- [ ] Other...

ท่านเลี้ยงกุ้งจำนวนกี่บ่อ *

- ( ) 1-5 บ่อ
- ( ) 6-10 บ่อ
- ( ) 11-15 บ่อ
- ( ) 16-20 บ่อ
- ( ) 21-30 บ่อ
- ( ) มากกว่า 30 บ่อ

ขนาดพื้นที่เลี้ยง *

- ( ) 0-3 ไร่
- ( ) 4-10 ไร่
- ( ) 11-15 ไร่
- ( ) 16-30 ไร่
- ( ) 31-40 ไร่
- ( ) 41-60 ไร่
- ( ) 61-80 ไร่
- ( ) 81-100 ไร่
- ( ) มากกว่า 100 ไร่
- ( ) Other...

ความหนาแน่นในการเลี้ยง *

- ( ) 1-30,000 ตัวต่อไร่
- ( ) 30,000-60,000 ตัวต่อไร่
- ( ) 60,000-100,000 ตัวต่อไร่
- ( ) 100,000-200,000 ตัวต่อไร่
- ( ) 200,000-300,000 ตัวต่อไร่
- ( ) 300,000-400,000 ตัวต่อไร่
- ( ) Other...

ปัจจุบันท่านใช้สารเคมีอะไรบ้างในบ่อกุ้งในระหว่างเลี้ยงและหลังเลี้ยง (ตอบได้มากกว่า 1 ข้อ) *

- [ ] Chlortetracycline (คลอโรด์เตตะไซคลิน)
- [ ] Oxytetracycline (Opsy, Oxy) (ออกซิเตตะไซคลิน)
- [ ] Tetracycline (เตตะไซคลิน)
- [ ] Ciprofloxacin (ซิโฟฟลอคซาซิน)
- [ ] Enrofloxacin (Eno-s) (เอนโรโฟลซาซิน)
- [ ] Norfloxacin (นอร์ฟลอคซาซิน)
- [ ] Oxolinic acid (กรด ออกโซ่โนลิค)
- [ ] Perfloxacin (เพอร์ฟลอคซาซิน)
- [ ] Misc. sulpha drugs
- [ ] Sulphamethazine (ซัลฟาเมตาซิน)
- [ ] Chloramphenicol (Chlor-M) (คลอแรมฟีนิคอล)
- [ ] Gentamycin (เจนตาไมท์ซิน)
- [ ] Trimethoprim (ไตรเมโทรพริม)
- [ ] Tiamulin (ไตอะมูลิน)
- [ ] BH one (บี เฮท วัน)
- [ ] Cinoxacin (Cenoxacin) (ซิโนซาซิน)
- [ ] Farmocin (ฟาร์โมซิน)
- [ ] Fomiquine (Flumequine) (โฟมิควิน)
- [ ] Gregacin (Coccidiostatica) (เกรกาซิน)
- [ ] ปูนขาว
- [ ] ปูนโดโลไมท์
- [ ] คลอรีน
- [ ] สีน้ำเทียม
- [ ] ฟอร์มาลิน
- [ ] Other...

ท่านได้ใส่ถ่านกัมมันต์ (Activated carbon) ระหว่างการเลี้ยงหรือไม่ *

- ( ) มี
- ( ) ไม่มี

ในระหว่างการเลี้ยง สารเคมีข้อใดที่ท่านพบและเป็นปัญหาต่อคุณภาพน้ำ (ตอบได้มากกว่า 1 ข้อ) *

- [ ] ไนไตรท์
- [ ] แอมโมเนีย
- [ ] ไนเตรท
- [ ] ไฮโดรเจนซัลไฟล์
- [ ] ไม่เป็นปัญหา
- [ ] Other...

ปัจจุบันท่านใช้ระบบบำบัดน้ำหลังจากการเลี้ยงแบบใดก่อนปล่อยน้ำเสียสู่ธรรมชาติ (ตอบได้มากกว่า 1 ข้อ) *

- [ ] ใช้ถ่านดูดซับ (Activated carbon, Charcoal)
- [ ] ใส่ยาฆ่าเชื้อ เช่น คลอรีน
- [ ] ปล่อยสู่ธรรมชาติโดยตรง โดยไม่มีระบบบำบัดน้ำ
- [ ] เลี้ยงระบบปิด ไม่ปล่อยน้ำเสียสู่ธรรมชาติ
- [ ] Other...

ปัจจุบันท่านจ่ายต้นทุนในการบำบัดน้ำเสียก่อนปล่อยสู่ธรรมชาติต่อเดือนจำนวนเท่าไหร่ *

- ( ) 0-1,000 บาท
- ( ) 1,001-2,000 บาท
- ( ) 2,001-3,000 บาท
- ( ) 3,001-4,000 บาท
- ( ) 4,001-5,000 บาท
- ( ) 5,001- 7,000 บาท
- ( ) 7,001-9,000 บาท
- ( ) 9,001-11,000 บาท
- ( ) มากกว่า 11,000 บาท
- ( ) Other...

ท่านคิดว่าต้นทุนในการบำบัดน้ำเสียก่อนปล่อยสู่ธรรมชาติต่อเดือนของท่านแพงไปหรือไม่ *

- ( ) ถูก
- ( ) ปานกลาง
- ( ) แพง
- ( ) แพงมาก

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PUBLICATION	Phuphantrakun, K. .; Chandrachai, A. .; Ekgasit, S. Amorphous Cellulose: Graphene Oxide Composite Bead. Trends Sci 2023, 20, 5496.