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COMPARISON OF SWELLING PROPERTIES OF ALGINATE BEADS CROSSLINKED WITH DIFFERENT CATIONS

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Master's Thesis

Supervisor

Assoc. Prof. Dr. Hakan KAYGUSUZ

İstanbul, 2025

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The thesis titled COMPARISON OF SWELLING PROPERTIES OF ALGINATE BEADS CROSSLINKED WITH DIFFERENT CATIONS prepared by YASEEN KHALID KHALEEL AL-ATTAR and submitted on 02/07/2025 has been **accepted unanimously** for the degree of Master of Biomedical Sciences.

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I hereby declare that this thesis meets all format and submission requirements for a Master's degree thesis.

I hereby declare that all information/data presented in this graduation project has been obtained in full accordance with academic rules and ethical conduct. I also declare all unoriginal materials and conclusions have been cited in the text and all references mentioned in the Reference List have been cited in the text, and vice versa as required by the abovementioned rules and conduct.

Yaseen Khalid Khaleel AL-ATTAR

Signature

DEDICATION

I dedicate this work to my father and mother. Also to all professors, academic staff, and lecturers in my great university; Altınbaş University. In addition, I dedicate this work to every person who guided and helped me in achieving this thesis.

PREFACE

I want to thank my advisor Assoc. Prof. Dr. Hakan KAYGUSUZ from the deep of my heart for all of his help, encouragement and kindness along this trip. The accomplishment of this task has been made possible by his expertise and constant support. I genuinely hope that all of his future efforts bring him happiness and success.

ABSTRACT

COMPARISON OF SWELLING PROPERTIES OF ALGINATE BEADS CROSSLINKED WITH DIFFERENT CATIONS

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Polymers are widely employed in many different applications, they are difficult to recycle and generally are not biodegradable. Scientific interest in creating biodegradable and biocompatible polymers has increased, especially for use in biology and medicine, because they come from natural sources, also they are non-toxic and environmentally benign, so we can make hydrogel from them. Superabsorbent polymers can be made by improving the characteristics of hydrogels, which are three-dimensional cross-linked structures with exceptional water retention. It plays important role in nutrients, medical, tissue engineering and protection of the environment, naturally occurring polysaccharide that is derived from brown algae and bacteria. It is essential in biological uses like wound healing, medication delivery and tissue regeneration because it has special qualities like gelling, moisture retention and film-forming capacity. Aqueous alginate solutions are preferred due to the biocompatibility and flexibility in crosslinking. Also, their mechanical strength, permeability and functional properties through the incorporation of organic and inorganic materials or the application of diverse crosslinking strategies. They combined with synthetic polymers demonstrate enhanced mechanical strength and healing properties, facilitating increased tissue regeneration and regulated drug release. Even with specific disadvantages like lower carrying ability, novel developments in alginate compounds are expanding their

uses, especially in the fields of renewable material development and wound healing. Alginate beads have been cross-linked using different cations, including calcium, which has strong antibacterial properties. Beads may affect the wound healing purposes and are increased by presence of certain particles, which have the ability to regulate or making small changes, typically, so as to improve it or take it less excessive to the immune system response and antibacterial properties. Flexible framework for creating biologically compatible substances have built-in antibacterial characteristics appropriate for a range of biomedical applications were provided using cation cross-linked alginate materials. In this study, 2% alginate solution was used for crosslinking with different cations to produce beads, these beads were applied by swelling test in different solution. And by comparing their antibacterial properties, the current study aims to figure out if the cation selection influences the antibacterial property of the beads and how they inhibit bacterial growth.

Keywords: Beads, Hydrogel, Sodium Alginate, Crosslinking, Swelling Test, Antibacterial Properties, Cations.

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ABBREVIATIONS

ALG	:	ginate
g	:	am
SAP	:	perabsorbent Polymer
SIF	:	nulated Intestinal Fluid
SGF	:	nulated Gastric Fluid
FTIR	:	urier Transform Infrared Spectroscopy
$CaCl_2$	:	lcium Chloride
$BaCl_2$	:	rium Chloride
$CoCl_2$	:	balt Chloride
$CuCl_2$	:	pper Chloride
$NiCl_2$	:	ckle Chloride
$FeCl_3$	:	n Chloride
$CeCl_3$	:	rium Chloride

LIST OF SYMBOLS

M.w	:	Molecular Weight
μ	:	Viscosity
λ	:	Wavelength
T	:	Transmittance
%	:	Percentage
m	:	Mass
m_i	:	Mass of Dried Beads
m_f	:	Mass of Swollen Beads

1. INTRODUCTION

Biomaterials were originally made to be inactive and not to interfere with the host's biological systems, they are obtained from nature and are frequently utilized to substitute tissues destroyed due to damage or illness. But because of their higher efficiency and other regular qualities above inherently produced substances, synthetic polymers, ceramics, and metal alloys have been replacing these types of materials [1]. Nowadays, the goal of creating novel biomaterials is to replicate a variety of human tissue extracellular matrix activities. These have the ability to control host reactions, and elements produced from nature are attracting a lot of interest again because of their innate biocompatibilit0y. So, because of its moderate gelation when divalent cations are added, the low toxicity and biocompatibility, and affordability has been studied and employed in a wide range of biomedical applications. Furthermore, by using a variety of cross-linking techniques they have numerous uses in transplanting cells, healing wounds and for the administration of bioactive substances like proteins and tiny pharmacological medications [2]. Alginate dressings reduce bacteria growth at the area of injury to promote wound repair and provide a physiologically wet atmosphere. Alginate gels have a wide range of uses in the pharmaceutical industry since they can be surgically injected or delivered by mouth. Hydrogels serve to regulate the shape and function of the manufactured tissue, transport cells to the correct location and give an environment for the development of new tissue [3]. Creating fresh substances to provide components with an extensive variety of characteristics that are appropriate for multiple purposes. The effective substances that can react quickly to modifications, and hydrogels that can hold water. We can better comprehend the efficiency of polymers and noticing the reaction to these composites by knowing the host reaction of inserted substances [4]. The development of the traditional definition of biological materials requires a conceptual change in the way these substances are characterized. So, when studying the polymers we would continue to discuss new and upcoming biomedical ideas [5].

1.1 ALGINATE

Alginate is a polymer made from brown algae, it is like cellulose in that it provides plant rigidity and adaptability. It is produced primarily from algae and makes permanent polymers when combined with cations like Calcium and Sodium, as in the Figure 1.1 [6]. It is a cheap, organic polymers extracted from algae. It is important to use in alginate-based scaffolds, that shows a great deal of promise for usage in several medical fields, include dermatological development. To increase its flexibility and promote cell attachment and support, alginate is commonly mixed with other polysaccharides. The general shape of hydrogels impacts on viability as medical supplies by how well they work in a given application. The M.w of the polymer chains connecting two adjacent cross-links, the associated net dimensions and the actual network strength are three most crucial characteristics employed to describe the network structure of hydrogels include equilibrium-swelling concept, rubber-elasticity model can be used to calculate the variables. Cross-linked hydrogel networks are currently described using a novel substitute. The unaffected cross-linkable compounds were defined and measured in a covalently cross-linked, swelling hydrogel network is made possible by excellent quality rotational spectroscopic [7].

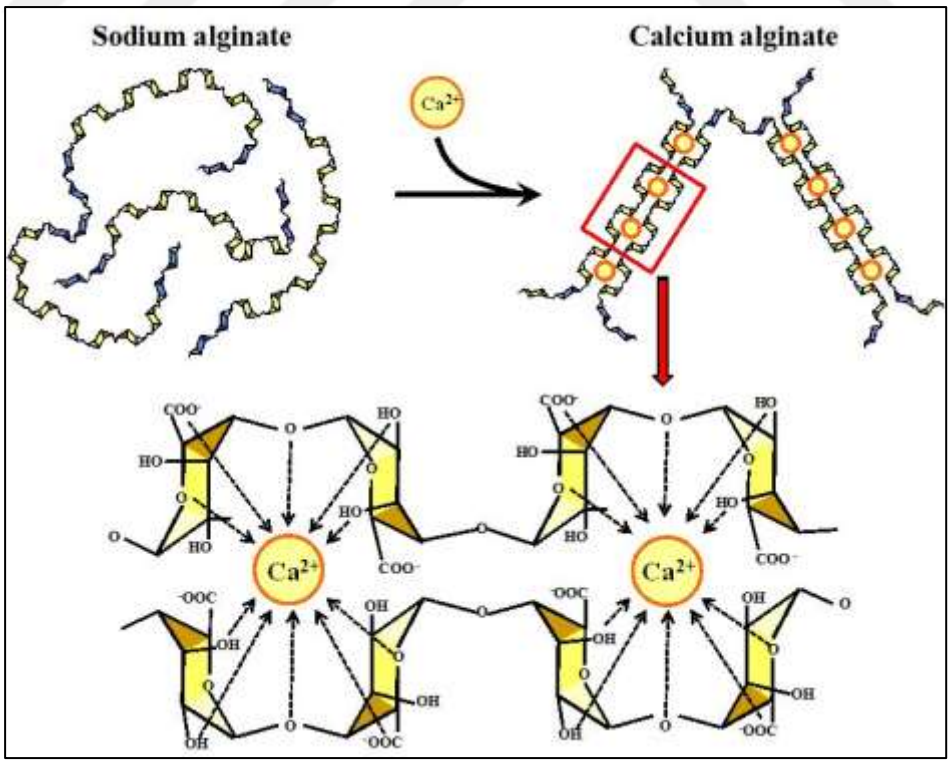

Figure 1.1: Positive Charge of The Ca^{2+} Combines with COOH.

1.1.1 History

Alginate was developed in 1881 and produced from algae by water and acids. D-mannuronic and L-guluronic compounds were discovered before a very long time after initial research found its urinary acid elements [8]. The understanding of Alginate has been improved and it seems as a block polymers connecting its composition to physical characteristics. Also, other scientists said that alginate contains an acid called uronic acid and this acid occur separately with alginate. Additionally, this encouraged more investigations in the following years. D-mannuronic acid was found in dissolved gel materials as a result. By means of β 1, 4 bond, the uronic acid atoms in alginate and cellulose had the same type of connections. Furthermore, the green algae contains two parts of glucose: one that is formed by alcohol from a watery solution and one that is produced by acid from an alkaline known as algin [9].

1.1.2 Structure

Alginates are a class of straight linear composites made up of ß-D-mannuronic and α-L-guluronic molecules that have distinct structure and pattern. Alginate has been divided into 3 parts via part acid hydrolysis. One had approximately equal amounts of each of the components and was found to include a significant amount of MG monomer debris, other is two included essentially homopolymeric units of G and M. Alginate was determined to be a genuine block dimer made up of homopolymeric sections of M and G, known as M- and G-blocks, as well, scattered with alternate structural parts as in the figure.

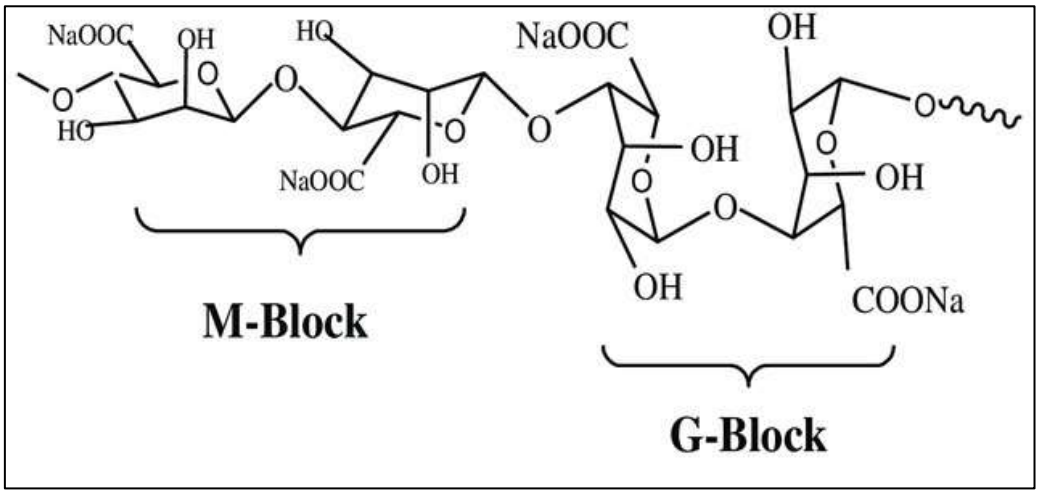

Figure 1.2: M-Block & G-Block.

When cations are present, alginate easily binds and creates a solid gel and the arrangement and content of the polymeric chain determines the rigidity, also affects the shape and dynamics [10].

1.1.3 Physical Properties

The physical characteristics of alginate that stand out particularly in comparison to different gelling polysaccharides are its ability to selectively attach multivalent cations. The nature of functional groups in the structure and the makeup and positioning of the two uronic acid groups in the structure all affect the physical properties of alginate [11]. In an acidic environment, polysaccharides undergo hydrophilic fragmentation. Some phases make up the process of acid hydrolysis of the glycosidic bond: first is the protons of the glycosidic O2 forms the combined solution. The breakdown of a compound into oppositely charged ions of the combined acid results in the creation of a stable side group and a carbonium-oxonium ion, and also the quick absorption of water to the carbonium-oxonium ion results in the formation of a reduced terminal group. Na-Alg may be kept as a powdery form out of direct sunlight especially in a cold, dry location. Keeping it in a refrigerator might extend its ability to stay fresh for a long time, Na-Alg is steady and breaks down quickly. It is believed that the carboxyl groups internal reaction is the cause of alginic acid's high proportion of breakdown [12].

1.1.3.1 Molecular weight

Alginate is a straight monomer, its strength and molecular weight and chain length are affecting on the state of thickness and semifluid. Depending on the need, alginates can be made using of many different kinds of typical molecules. Economically accessible Na-ALG typically have molecular mass of thirty to four hundred thousand g/mol [13].

1.1.3.2 Viscosity

Alginic acid is resistant in water and in chemical solvents, by raising the molecular weight of alginate may change to develop the mechanical features of them. But when it increases, it gets extremely viscous [14]. For instance, when proteins or cells are combine together in an Alg mixture and injected inside the human system, there will be a chance of injury. A salt of alginic with more MG blocks is solvent at nominal acidity levels, this relies on the

polymer shape. The mixture of high and low mass polymers might be changed to greatly improve gel flexibility while causing a small degree of rise in liquid velocity. Viscosity, setting times and suitability with dimensional consistency needs to be taken into account. The viscosity of a produced alginate imprint medium may be impacted by low viscosity characteristics. The absorption of the polymer on the capillary wall complicates the measurement of liquid viscosity in a diluted solution [15].

1.1.4 Production

Two species of bacteria and multiple types of brown seaweed can make alginate which are Pseudomonas and Azotobacter [16]. The separation of Alginate is based on the conversion of solid acidic ions in the cellular membranes of brown seaweed to liquid alginic acid or Ca-alginate. The steps of production include: Buffering and preliminary extraction and condensation. The alginic acid compounds undergo protons transfer using a powerful acid, such as hydrogen chloride to become pure of alginic acid, then solid alginic gets reduced and dissolved using an alkaline to create a water-soluble Na-Alg. Finally, Hydrochloric is dissolved by means of alcohol or calcium chloride to remove the substance from the solution used for extraction. Soluble alginates make it possible to produce goods with identical dimensions and structure and the mass manufacture of these items is greatly facilitated by uniformity of the reformed substance [17].

1.1.5 Alginate Hydrogel

Several cation pairs generate ionic gels, making them especially useful for food products and different sectors. Since swelling becomes easier by the joint interaction of G blocks and ions, the amount of G blocks in the alginate structure determines the binding capacity of Alginate. Particularly, Calcium is safe, so it is useful for formation of alginate [18]. Integration of the oxygen molecule with carboxyl chains maintains the egg-box structure which forms when Ca^{+2} links to G sites. Gel becomes harder when the G block concentration increases [19]. Alginic salt has a variety of uses, such as cellular immobility in the field of biotechnology medication preparation in medical products and the process where vitamins, minerals, antioxidants etc. are enclosed with protective material to improve stability and functional properties. The Chemical and physical cross-linking methods, including covalent bonds, ionic contact, molecule attachment among other processes that are capable of producing

alginate hydrogels. Gel hardness and homogeneity are influenced by temperatures, gelation rates and diffusing. The oxidation and phosphorylation are examples of chemical alterations of alginate that improve its rigidity and stickiness. They are demonstrating an extensive variety of potential uses as polymers and they have served in fundamental investigations in biology and scaffolds for tissue engineering and drug delivery systems [20] . The polymeric system composed of just one type of monomer fundamental structure in every poly network is defined as a 'Homopolymeric gel'. The type of molecule as well as the method of polymerization can determine whether the homopolymer has a connected skeleton. A number of distinct polymer groups having more than one aqueous element, organized randomly in blocks or alternately throughout the monomer network's chains, make up copolymeric hydrogels [21].

1.1.6 Applications of Hydrogel

The biggest use involves biodegradable sanitation items like feminine towels, adult's urinary items especially baby diapers. Additionally, it is crucial to both farming and woodcraft, when utilized as surface additives, SABs enhanced nutrient preservation, decreased crop mortality, boosted plant development rates and decreased rainwater usage [22]. In comparison with fine sand or other material carried by running water and deposited as a sediment and abundant gound sand containing organic component formed by decomposition of materials, these improved the light yellowish brown soil ability to retain water and nutrients [23]. The shape, volume, flexibility, appearance, vaporization and absorption of liquids are all specifically affected by SABs employed in soil. Since superabsorbent is incredibly effective at improving soil conditions, saline that include water and soils remain challenges [24]. Excellent qualities, such as substantial amount of water, smooth and have a tough elastic texture regularity and reduced tension when in contact with water or biological solutions, make them useful in both the scientific and drug sectors. When contrasted to different artificial substances, these polymers show physical characteristics that are comparable to those of living tissues [25]. SABs are great choices for a wide range of bio-related purposes due to their watery and largely benign innate, which frequently results in reduced unwanted attachments to enzymes and organelles. They're specifically utilized in a device that use a biological molecules called biosensors, regulated pharmaceutical delivery networks, ligament regeneration, flexible contact lens and blood- contacting polymers [26].

1.1.6.1 Food applications

Alginates were confirmed to be harmless and have been acceptable for usage as nutritional supplements [27]. Additionally, they are employed as foods covering materials and eatable films to extend the item's protection, longevity and strength. Alginate-based nutrient additives demonstrate exceptional durability, mobility, rip obstruction and ability of substance to resist oil or preventing it from absorption qualities. By adding anti-bacterial elements to its structure, alginate gels are shown to provide an effective defense versus bacterial degradation of herbs and meat [28]. Furthermore, because of the gel formation and thickness, they are utilized as inhibitors and thinners.

1.1.6.2 Biomedical applications

Gel has several uses in healing injuries, the administration of bioactive compounds including medications and amino acids and transplantation of cells because of their resemblance to the outside layer that surrounds living organs [29]. Alginate dressings decrease the bacteria in the injured region, promote wound repair and create a physiologically wet atmosphere. They are also utilized in regulating the absorption of a variety of pharmacological compounds, ranging in size between micro to massive. Medicine incorporation in the framework of gels and its expulsion can be precisely regulated because of the great swelling potential and permeable nature. In terms of medication delivery, it is used for controlled dispensing of cutaneous, protein medications, ocular and orally. Additionally, it is used for cell transport in the restoration of bone, liver, cartilage, nerve tissue and vessel. Alginate biopolymers including clay are being utilized to deliver vitamins [30].

1.1.6.3 Wound dressing

Polymers mostly exterior contact with the body have a very broad range of applications in wound dressings. For the situation of late recovery with long-term injuries, several stages of the complicated biochemical procedure for wound repair, that includes irritation, cell fragment removal, movement, growth, division and transformation can get disrupted [31]. In order to assist biological treatment or eliminate adverse effects, new bioactive copolymer wound care products incorporating discharge or adsorbed qualities were created. Compared to conventional cotton covers, these are additionally easier for the individual receiving treatment [32]. The bandage must allow H2O and O2 to pass through in order to promote

wound recovery in a way that prevents harmful germ enter the wound and cause damage. Dressings with hemostatic qualities are recommended, particularly when excessive stress is present. For diverse wound categories, a broad variety of artificial, natural or mixed substances have been used in various forms. Although clear impermeable coatings sustain humidity at the location of injury and offer mechanical defense and an obstacle, these may not be appropriate for highly bleeding or infected areas [33]. The components that give durability are rubber, water soluble protein and soluble gelatinous polysaccharide and alg. These may have designed to have release of medications capabilities for steroids and antibiotics means they are ideal for wounds that bleed simply. Although they are very resilient and made of protein and hypoallergenic alginate or chitin or artificial hydrogels are typically required mechanical assistance. So, they wouldn't be appropriate for extensively leaking infections since they have begun to retain a lot of fluids though they can be employed for releasing drugs, revive dried cells and aid in a wound that undergo a natural process where the body uses its own enzymes to breakdown and remove dead tissue. Wounds from fire and even persistent injuries like sore that developed by sick person because pf pressure caused by lying in bed in one position are frequently treated with polymer dressing based on superabsorbent. Because of its great degree of versatility, polymer treatments may be put to injuries anywhere on the human body. When used, they are very simple to take off and do not bring harm for the person. Gel dressing for wounds were known to promote healing and rebuilding as well as to being simple to apply and remove. This is because the hydrogel's high water content helps create a humid conditions on the area of injury and this is thought to be optimal for cell growth and skin renewal [34].

1.1.6.4 Environmental applications

In ecological uses depend on their ability to trap cationic and conductive ion thanks to their abundant effective units. The interaction among linking electrons and contaminants is how this extraction happens. Metallic substances, commercial pigments, antimicrobial agents and other contaminants were thoroughly investigated for extraction, which are inexpensive and incredibly effective absorbents.[35]

2. LITERATURE REVIEW

B. Orhan examined improving the swelling capacity of natural hydrogels that are biodegradable and biocompatible in order to create a superabsorbent substance [36]. A material that may biodegrade and be utilized for surgical devices with no damaging cells was created utilizing alginate and CMC and were used to create a substance capable of being decomposed by bacteria or other living organisms and a material used to surgical implants not harmful to living tissue. The compound that contains 2% Alginate and 2% CMC crosslinked with into 3% Calcium Chloride solution. Swelling response was examined by using citrate-buffered solution, simulated intestinal fluid, simulated gastric fluid and pure water. Swelling level enhanced when CMC was added, and quasi-cryogel beads demonstrated superabsorbent qualities, so it was between 56% - 960% because CMC has hydrophilic carboxyl groups. Ordinary beads swelled from 960%-1650% with quasi-cryogel. Also, in saline solution expanded by 1850-2350%. And in SGF solution between 150% -310%, because of the pH value 1,2. Because of their porous structure, quasi-cryogel beads have been seen to dissolve faster than regular beads due to fast swelling process. It has been found that superabsorbent spheres retain their ability to inflate even after several uses. According to the result, the highly absorbent polymers can be used in controlling nutrition, farming, pollution and health care.

Reshma G. et al [37], regarding application in feminine hygiene pads, a biodegradable superabsorbent material comprising starch and cmc was produced. The membrane was created using two membranes manufacturing procedures (freezing-drying and stage reversal), after cmc and starch were cross-linked using a mixture including Sodium trimetaphosphate and Aluminum sulphate with a 1:1 by mass proportion. The CMC-starch membrane produced by exaltation, which involves chilling materials, lowering ambient force, followed by using heat to remove liquid, and because of its extremely spongy construction, it demonstrated rapid intake qualities and blood holding abilities. This type of membrane has a 30 g/g water holding ability and 20 g/g blood storage potential. When comparison to the feminine hygiene pad that is sold for business, this demonstrated greater ability for absorbing.

Peng, N., Hu, D., Zeng, J., Li, Y., Liang, L., & Chang, C. [38], Carboxyl methyl cellulose and clay gels were made with excellent structural effectiveness, excellent pigment removal effectiveness with superabsorbent qualities. At 10 mg/L and 100 mg/L, the elimination efficiency of methylene blue was determined by 96.6% and 98%. In order to remove colour from sewage, cellulose-clay compound gels demonstrated a strong absorbent property.

Ciolacu, D., Rudaz, C., Vasilescu, M., Budtova, T. [39] In this study, Epichlorohydrin was used to crosslink cellulose hydrogels with Sodium Hydroxide 8% and water to examine their swelling activity. The effects of mechanical and chemically gel formation on the swelling of cellulose hydrogels in fluid following production and freeze-drying cryogels as well as the density, anatomy and construction. Additionally, the potential of preserved in the freezer cellulose hydrogels as carriers for drugs was investigated. Procaine HCl was put into cellulose hydrogels and the mechanisms of its dissolution within the fluid were examined. Increasing of hydrogel swelling degree with the increase of ECH concentration, maximum swelling being at approximately cellulose: ECH stoichiometric ratio. minimal swelling of cryogel is around 900 % and the maximal is around 2500 % while for hydrogels it is 1300 % and 3500 %.

E. Motamedi, B. Motesharezedeh, A. Shirinfekr, S. M. Samar [40] NC powder, ball-milled natural chars and chemically modified NC nanoparticles were synthesized and then utilized as fillers for preparation of starch-g-poly(acrylic acid- co-acrylamide) superabsorbent composite. The goal of this study was to assess natural char's efficacy as an economical and biodegradable solution for creating powerful superabsorbent polymers using starches. The morphology and surface functionalities of the as synthesized fillers and their composites were scrutinized using FTIR, FESEM, elemental mapping, AFM, Boehm titration and TGA analyses. NCNPs with the smallest particle sizes (14.8 ± 3.0 nm) and the highest oxygen functionalities were selected as the best filler candidates. The NCNPs/Hydrogel nanocomposite's two-fold absorption of water (389.9 g/g) in contrast to the regular hydrogel (202.1 g/g) may be explained by the simultaneous presence of physical and covalent cross-linkage. Compared to dry polymer 7.1%, this hydrogel kept 3 times as much liquid 23.1% after fourteen days. Every synthetic compound adhered to a statistical method for explaining how substances behave when they swell in a certain media and water molecules move through a material due to a concentration gradient. Its biological nature and

water-holding ability would increase the possibility of uses as a sustainable and cost-effective commercial gel.

Z. Wang, A. Ning, P. Xie, G. Gao, X. Li, L. Xie, A. Song [41], the water absorbency of the HSAR increased with increasing the content of Graphene oxide when the content is lower than 0.6 wt%. The highest swelling ratio for the hybrid hydrogel with 0.6 wt% of GO is 750 gg^{-1} in distilled water and 85 gg^{-1} in 0.9 wt% in NaCl solution. Incorporation of moderate amount of GO into the CMC-based SAR matrix can enhance the water absorbency. The swelling ratio of the two tested samples significantly increased as the pH value increased when the pH value was less than 5. Pure SAR, which attained a rather stable platform with very slight vibration, the rising stream of the swelling ratio of the two samples clearly reduced when the pH value was raised steadily from 5 to 7. At pH 7, the swelling ratio reached its highest value. The swelling ratio of the two tested samples significantly decreased as the pH was raised from 7 to 12. The natural composition was not visibly affected by the addition of graphene oxide, the hybrid superabsorbent resin demonstrated better swelling proportion, increased temperature resistance, and water-retention capacity.

When the pH < 5, most of the COO group changed into COOH groups, so the repulsion between polymeric chains decreased, leading to a decrease of water absorbency. When the pH > 10, most of the COOH groups converted into COO groups, and the screening effect of the counter ion (Na+) on the poly-anionic chain is more evident, which also led to a decrease of the water absorbency. This phenomenon indicated that the buffer action of COOH and COO disappeared when a large amount of acid or base is added. When the pH values kept in the range of 5–10, some of the carboxylate groups were ionized and the ionization degree of the carboxylate groups remains almost constant, which induces a similar osmotic pressure between the hydrogel network and the external solution. When the CMC amount was increased from 5 to 12 weight percent, the HSAR's water absorbance marginally increased. The viscosity of the reaction fluid clearly increased as the CMC increased, which limited the remaining reacting substance’s ability to flow freely and distribute evenly throughout the reaction system. As a result, the connected copolymer chains molecular weight and grafting performance both dropped, which in turn caused the swelling ratio to drop. As the amount of crosslinker became from 0.01 to 0.05 weight percent, the fluid sensitivity raised as well. The highest absorption of water was attained at 0.05 weight percent crosslinking compound.

This situation is caused by the reason that when the quantity of crosslinker was less than 0.05 weight percent, the volume of solvent rose and the HSAR's three-dimensional structure was unable to develop effectively, resulting in a reduced swelling ratio. More cross-linking sites were created in polymerization, which raised the cross-linking concentration and reduced the volume of the polymer multidimensional network, when the cross-linker concentration rose over 0.05 weight percent. Therefore, it was not advantageous to enlarge the structure and store a lot of water. Therefore, this type of hybrid SAR, which combines the superior qualities of SARs with the special qualities of GO, may be widely used in many applications.

Ajaman A., Azizon K., Pairote K. [42]. In order to create SAPs and SAPC with high water expansion rate and biodegradability, and for production, 99% pure acrylamide was utilized, the polyacrylamide was grafted onto a cellulose derivative using liquid copolymerization. Through physical combining with epoxidized natural rubber, bentonite clay was added to SAPC in order to aim for water-swellable rubber. The maximum swelling capacity was over 426 g/g and 538 g/g for the SAPs and SAPCs. Swelling capabilities in saline solution were almost four times lower than those in pure water. FTIR spectrum of HEC showed a broad band at around 3560-3320 cm^{-1}, strong absorption peak at 2883 cm^{-1} was attributed to primary –OH bending vibrations of Ethyl hydroxyl. So, HEC grafted with PA and related bentonite clay was used to create a superabsorbent polymer with its compounds.

E. Susilowati, L. Mahardiani,R. D. Hardini [43]. This research used a chemical treatment approach to create and evaluate Silver alginate nanocomposite layers. It examined how the amount of Ag nanoparticles affected the structural, physical, antibacterial, mechanical characteristics of material with an emphasis on the potential uses in antimicrobial manufacturing and medicine. Roughness and permeable form of a nanocomposite films was discovered by Scanning Electron Microscopy investigation. Gram-positive bacteria were more susceptible to the restrictive effects of films compared to the negative. The diffusion technique was used to determine the antibacterial properties of silver-alginate nanocomposite films over gram-positive (S. aureus and MRSA) and gram-negative (E. coli and ESBL) bacteria. The results indicated by the range 401.01–409.00 nm of wavelengths in the ocular spectrum, and diameter was between 2 - 23 nm. The feature and ability to effectively combat bacteria that are resilient to drugs, demonstrate the opportunity for use in

antibacterial products and medicine. The sample restricting area on the growth of bacteria was observed in order to do the evaluation. Before making the antibacterial test medium, the resultant film was sliced into a circle to conduct the antibacterial analysis. Nutrient Broth solution mixed in water at a level of 0.8% w/v and used as bactericide environment. So, it may use in antimicrobial packaging in the medical industry.

Chang, C., Duan, B., Cai, J., & Zhang, L. [44]. The purpose of this work was to use Epichlorohydrin as a cross-linker to create carboxymethyl cellulose. Hydrogels in an aqueous NaOH/urea environment, swelling ratio was nearly 1000. Hydrogels demonstrated intelligent expanding and decreasing in aqueous solutions of NaCl or CaCl2. Swelling ratio of the cellulose/CMC hydrogels increased rapidly with an increase in the CMC contents. Highly hydrophilic carboxyl group of CMC could absorb a lot of water to enhance the space in the hydrogels. The entanglements of cellulose chains through hydrogen bonds could occur easily in solutions of high cellulose concentration, leading to the decrease of the equilibrium swelling ratio with an increase of cellulose content. In NaCl solution, the swelling ratio of hydrogels decreased with an increase of the ionic strength of the solution. The hydrogels with higher CMC contents exhibited more significant decline of swelling ratio with the increase of the NaCl concentration. In $CaCl_2$ aqueous solution, the swelling ratio decreased quickly because of the higher cationic charge of $CaCl_2$. Shrinking kinetics of the cellulose/CMC hydrogels in NaCl aqueous solution at 37 C., all of the swollen hydrogels tended to shrink and lose water once transferred into NaCl solution. However, the water retention of the hydrogels decreased 53% - 28% after 3 h with an increase of CMC content. The hydrogels possessed smart behaviors of swelling and shrinking in physical saline water, which will be very important for applications in biomaterials.

Alam, M. N., Islam, M. S., Christopher, L. P. [45] Carboxymethyl cellulose was originally created by reacting cellulose with Na monochloroacetate and subsequently it was cross-linked using ECH. 725 g was the amount in developed hydrogels retaining capacity in distilled water, this is equivalent to the industrial manufactured polyacrylate solvent keeping rate of up to 1,000 g/g and far higher than any other readily accessible superabsorbent cellulose-based product that holds water ability of 10−100 g/g. The highest possible water retention level achieved in saline water with 0.9% sodium chloride was 118 g saline/g, over two times the liquid holding ratio found in industrial gels, which are about 45 g/g. The

number of COOH whereas total Mw were ascertained using chemical study then the hydrogel synthesis conditions were improved. X-ray diffraction, Fourier transform infrared spectroscopy and SEM were used to analyze the native superabsorbent hydrogel. After 4 round of reuse, the hydrogels exhibited acceptable re-swelling with reducing 10% of their capacity for absorption into distilled water. The new hydrogel may continue with their artificial equivalents in areas like important hygienic and medical supplies due to their better swelling characteristics in saline solution.

Capanema, N. S. V., Mansur, A. A. P., de Jesus, A. C., Carvalho, et al. [46] The development of healthy, sustainable material that can be used as wound dressings and skin substitutes were the main goals of this investigation. These films were made from CMC derivatives that were scientifically crosslinked by Citric acid and improved with Polyethylene Glycol through a sustainable water-based technique. The degrees of swelling about 4000% occurred in superabsorbent hydrogel, FTIR spectrum of PEG the broad band in the 3700–3000 cm^{-1} region assigned to vO-H vibrations and the peaks at 3000–2800 cm^{-1} related to vC-H bands. For CMC, the major vibrational bands related to carboxylates (COO^{-}) asymmetric (1600 cm^{-1}) and symmetric (1416 cm^{-1} and 1324 cm^{-1}) stretches. Hydrogels have been developed having characteristics which may be adjusted by extending crosslinking such as absorbing significant volumes of water. So, hydrogels are seen to be attractive superabsorbent with important qualities for supporting wound healing and renewal, especially given their growing potential as a future class of alternatives to skin in the care for long-term infections.

Gayet, J.-C., & Fortier, G. [47] Structural features of a biopolymeric hydrogel made by cross-linking activated PEG mass of 8000 with Bovine Serum Albumin. This hydrogel expands a lot when it swells and contains a lot of water about 95.5%. The Albumin-Glycol hydrogel exhibits excellent mechanical qualities with having an excessive water percentage. Because of its elevated degree of elasticity, it is capable of taking a lot of pressure until shattering. This rigidity is preferred for surgical dressings or promoting biopolymers and is rare in substances with a lot of liquid, comparable equivalent was seen when inflated molecules containing pure polyethylene oxide or within the presence of free PEG. Main characteristics of the hydrogel are caused by the residual water, which is accessible throughout the polymer structure. So, the discharge of methylene blue illustrates how

bacteria diffuse across it and this kind of polymer makes an excellent choice for products with controlled release.

B. Orhan, H. Kaygusuz, F. Bedia Erim [48]. Polymer mixture including 2% CMC and 2% Alginate crosslinked with Calcium. The beads were transformed into QuasiAlgCMC beads via the quasi-cryogelation process, which involves significant freezing at -21 C. The degree of swelling was evaluated in various solutions. Because of an important modification in the bead structures during the freezing procedure, the swelling level of beads increased significantly. In pure water and simulated gastric fluid and isotonic solution, the QuasiAlgCMC beads increased in order of (1652%, 2343%, 309%). So, this leads to the potential of drug delivery. The beads also swelled 2318% in Citrate-Phosphate buffered saline and 2294% in intestinal fluid, but many broke down after thirty minutes. Absorption of 2343%, after five cycles it was 1200%, and the crosslinker content 3%, 5% $CaCl_2$, the swelling proportion of the beads was (1847% ,460%). The beads with 1:2 (Alg:CMC) and 2:1 swelled in isotonic solution 1082%, 750% ratio of 1:1 which swelled 1847%. Alg beads swelled 60% in pure water, and 197% in isotonic solution, and 90% in SGF, 1683% in SIF (at 90 min) and 2066% in Citrate-PBS (at 240 min) The result of this experiment demonstrates the effective fabrication of QuasiAlgCMC beads and their superabsorbent abilities. Hydrogel shape altered and their fluid retention capabilities significantly improved due to the simple quasi-cryogelation process. So, the ability to maintain a certain level of superabsorbent that used for many purposes, including the elimination of contaminants from water and the manufacturing of diapers.

Batista, R. A. et al. [49]. The potential for creating affordable, sustainable biopolymer-based superabsorbent hydrogel with high stability and swelling capacity, Chitosan, Xanthan gum, and Alginate have been used with distilled water, and 2% Lactic acid mixture was used to dissolve the chitosan. Distilled water was used to dissolve the xanthan gum or alginate. For 24 hours, the polymers were maintained independently at 25 ±1 °C. while being mechanically shaken. The polymeric particles were combined and agitated for 24 hours at 25 ±1 °C. Glycerol 40 (w/v) was added in a solution. For more than 2 days at 65 ± 1 °C., 3 mL solution was dried in a warm oven then placed in Petri dishes. After five minutes of immersion in a NaOH solution 1 mol/L, the dry surfaces were wiped with filter paper for three minutes, this procedure was carried out ten times, followed by 12 hours immersion in

0.1 mol/L NaOH solution, followed by a neutralizing rinse with distilled water. After that, the samples were freeze-dried. As a result, Chitosan has a strong influence on the maintenance of hydrogels structure after swelling around 3000% of acidic fluid absorption after 24 h. In an acid environment, reached 1665%, 2024%. At pH 7.0 it was 1005%, 667%. With swelling degree lower than 200% after 24 h. C1G2 180%, C1A2 136%. Highest swelling degree results were achieving 3046%. And C2A1 1592%. In FTIR-8300 spectrometer at 25 °C, were 4000 - 400 cm^{-1} with sensitivity 8 cm^{-1}. This substance is appropriate for application in the food and pharmaceutical sectors, such as in disposable diapers and food packaging.

Yan Hu, Tao Chen, Xiaoying Dong, Zhinan Mei [50]. A mix of chemical and ionic cross-linking techniques, new biopolymer hydrogels made of Sodium Alginate and Oxidized Sodium Alginate that have a polymer made up of multiple chains. Utilizing sodium cation and the Periodate anion, oxidative Na-Alg was produced with Na-Alg. Sodium alginate structure was cross-linked by calcium ions and the other was cross-linked by oxidized sodium alginate. As a swelling process the 2300 is the inflating rate of the beads, and the production circumstances and acidity had a significant impact on their expanding characteristic. Compared to the natural Na-alg over calcium structure. The pH-sensitivity and stable beads will make an excellent choice to the regulated medication delivery.

Yan H., Mengzhu z., x. et al. [51] . Making of hydrogel beads using organic polysaccharides was the goal of the current investigation. By using Ca-alginate polymeric mechanism, Hyaluronic acid & Chitosan have been effectively combined through multiple crosslinking. The preparation process involved obtaining a mass percentage of 2:1 between 2% Alginate salt and Hyaluronic acid. For the crosslinking procedure, the combination was dropped on the Calcium liquid, and Polyelectrolyte crosslinked for one and a half hour using 2% Chitin. By varying the amount and mass proportion of chitosan and hyaluronic and Na-Alg, the ideal composition was obtained. The time period for the greatest swelling level was increased to 7.5 hours, and the swelling percentage at pH 7.4 was raised to 120. When comparing with the basic sodium alginate and calcium structure, the swelling response was noticeably better. Thus, the initial results definitely indicate that these hydrogel beads of CS, HA and SA could be an acceptable choice for biomedical delivery systems.

Yan Hu, Jing Peng, Lei Ke, Dan Zhao, et al [52]. The production of pH-sensitive hydrogel bead as delivering medications using Carboxymethyl Chitosan with Na-Alginate. A chemical method to synthesize microparticles based on electrostatic interactions between ions with different charges were used to create these compounds hydrogel beads. Na-Alg and Calcium undergo a cationic gelation, and also CMCS with β-Sodium glycerophosphate. Thermogravimetric testing, infrared analysis and SE imaging were used to analyze the structural characteristics of hydrogel beads. So, when the quantity proportion became 1:2 with the concentrations of sodium alginate and carboxymethyl cellulose chitosan were 3%, the beads crosslinked with glycerophosphate and Calcium Chloride mixture increased to 31.2 times faster and take about ten and half hours to fully expand. Bovine serum albumin is being used for distribution of drugs. As a result, at pH 1.2 the BSA discharged from the beads with a release proportion 10%. The whole releasing duration was raised to 11 hours at pH 7.4. The mixed hydrogel exhibits an acid tolerance with prolonged absorption characteristics making it useful for orally delivery of medications.

Ting Guo, Ning Zhang, Jinbao Huang, et al [53]. Here, the Alginate/gelatin core-shell spheres were made using a one-step melting technique to increase the alginate's usability and persistence. The internal structure was made of gelatin cross-linked with glutaraldehyde and the outer layer was made of sodium alginate. To assess how the Na-Alg layer affects the in vitro drug release characteristics, Metformin hydrochloride salt and Indomethacin were used, also swelling test and SEM and FTIR were used to investigate the structure and characteristics of several core-shell beads. This study has demonstrated that these beads have a visible core inside and an outer protective barrier that firmly covers the outside. The microsphere's heat resistance was enhanced by the core-shell framework using a Na-alginate shell and the proportion of storing was 90%. Thus, when the amount of glutaraldehyde rises, the rate of swelling was reduced. And when passed the 360 min., the total absorption of an anti-inflammatory medication in hydrochloric acid solution reached 8.7%. So, according to this study, the beads swelling characteristics and release of drugs characteristics enhances by the core-shell construction.

Haniyeh M.j, Aleksey D. Drozdov, et al. [54] . To decrease the ionization of carboxyl groups on alginate structure, HCl was added to alginate mixture 1% to bring its pH down to 3.5. the 50 ml of CaCl2 liquid combined with alginate mixture in a 28:1 (v/v) ratio. To create an

ineffective gel, the combination was put onto a container and allowed to dry at room temperature for a day, and the hydrogels were submerged for two days in various solvents to finish the cross-linking procedure. So, it was discovered that cations have an impact on the reduction and retention proportions. Then, the samples were placed in pH 7 and it was seen that Iron possess a greater impact on elasticity than other ions. Copper > strontium = calcium > zinc is the pattern in which the modulus of elasticity of polymeric hydrogel connected with divalent ions reduces. The flexibility of ionically cross-linked alginate polymers depends differently on the final amount of swelling than the traditional theory predicts for chemically cross-linked gels.

Yue Z., Qiumin M., Faith C., P. Michael Davidson, et al [55]. The present research intended to determine how adding soybean oil affected the antibacterial and physical characteristics of alginate film that made by 1% or 2% of cinnamon bark oil. 8 grams of Na-Alg were dissolved in 400 milliliters of distilled water at 70 degrees Celsius to create 2% alginate. CaCl2 0.05 g/g alginate was mixed in to reinforce the material, and glycerol 0.3 g/g alginate was used as a softener. CBO was mixed with tween 80, and after that, SBO was included to the combination in varying amounts. The film-forming solution was completed by adding distilled water until the last alginate level was 1% w/v. As a result, the thickness of film ranged from 0.021 to 0.045 mm. So, Alginate films with soybean and cinnamon bean oil have the ability to enhance the quality and bacterial safety for consumable food items, and can enhance specific physical attributes and antimicrobial effectiveness of food films include natural oils.

Table 2.1: Comparison of Previous Studies.

Author	year	Material	Result
B. Orhan	2021	Alginate, CMC, CaCl2, SGF, SIF, Saline solution, citrate-buffered solution	When CMC was added swelling was 56% - 960%. 960%-1650% with quasi-cryogel. In saline solution expanded by 1850-2350%. And in SGF solution between 150% -310%
Nair, S. V., Menon, D.	2020	Starch, NaCMC, and mixture of Sodium trimetaphosphate & Aluminum sulphate crosslinker	Rapid intake qualities and blood holding abilities. This membrane has a 30 g/g water holding ability and a 20 g/g blood storage potential. This demonstrated greater ability for absorbing.
Capanema, N. S. V., Mansur, A. A. P., de Jesus, A. et al.	2018	CMC, PEG , Citric acid.	Expanding rates 100% to 5000%. Demonstrated tissue death over 94 % and proved the non-toxic property to cell and promote cell adhesion and support.
Peng, N., Hu, D., Zeng, et al.	2016	CMC, Clay	The elimination efficiency of methylene blue was determined by 96.6% and 98%. Cellulose-clay compound gels demonstrated a strong absorbent property
Alam, M. N., Islam, M. S., et al	2019	CMC , ECH, purified water, isotonic solution, MCA, HCl, NaOH, ethanol	In deionized water the swelling was 725 g/g, and in saline solution it was 118g/g.
Diana C., Cyrielle R., et al,	2016	Cellulose 8% NaOH-water, ECH, PrHy.	Increase of hydrogel swelling degree with the increase of ECH concentration, maximum swelling being at approximately cellulose:ECH stoichiometric ratio. minimal swelling of cryogel is around 900 % and the maximal is around 2500 % while for hydrogels it is 1300 % and 3500 %

Table 2.1: Comparison of Previous Studies "Table Contunied".

E. Motamedi, B. Motesharezedeh, A. Shirinfekr, S. M. Samar	2020	Natural Char, BMNCs, NCNPs, starch -*g*-poly(acrylic acid-*co*-acrylamide) superabsorbent composites. 98% H_2SO_4, 30% H_2O_2, $KMnO_4$, $C_6H_{10}O_5$, 98% AM, 99% AA, 99% MBA, 98% APS, 85% KOH, 98% CH_3OH,	The composite performance was controlled by the filler's properties. NCNPs with the smallest particle sizes (14.8 ± 3.0 nm) and the highest oxygen functionalities were selected as the best filler candidates. The addition of NC and BMNC in the polymer matrix could not significantly improve the water absorption performance of the composite. Gel strength of samples displayed the following descending order of NCNPs/Hydrogel > BMNC/Hydrogel > NC/Hydrogel > neat hydrogel > commercial hydrogel. NCNPs/Hydrogel nanocomposite showed three-fold water-retention capability compared with the neat hydrogel (23.1 % vs. 7.1 %)
Zhimin W. ,A. Ning, P. Xie, G. Gao, Xin Li, Lixia Xie, A. Song	2017	GO, AA , Ammonium persulfate, CMC and N,N-methylene bisacrylamide	Absorbance increased with increasing the content of GO when the content is lower than 0.6 wt%. Highest swelling ratio for the hybrid hydrogel with 0.6 wt% of GO is 750 g g^{-1} in distilled water and 85 g g^{-1} in 0.9 wt% in NaCl solution. The rising stream of the swelling ratio of the two samples clearly reduced when the pH value was raised from 5 to 7. At pH 7, the swelling ratio reached its highest value. The swelling ratio of the two tested samples significantly decreased as the pH was raised from 7 to 12. HSAR demonstrated better swelling proportion, increased temperature resistance, and water-retention capacity.

Table 2.1: Comparison of Previous Studies "Table Contunied".

Ajaman A.,Azizon K., Pairote K.	2017	KPS, MBA, SAPs, SAPCs, HEC, AM,	Maximum swelling capacity was over 426 g/g and 538 g/g for SAPs and SAPCs, FTIR spectrum of HEC showed a broad band at around 3560-3320 cm^{-1}, strong absorption peak at 2883 cm^{-1} was attributed to primary –OH bending vibrations of HEC.
E. Susilowati, L. Mahardiani, R. D. Hardini	2022	Alginate, Silver Nitrate, CH3COOH, NaOH, S. aureus, Methicillin Resistant Staphylococcus Aureus, MRSA, E. coli, Extended Spectrum βLactamase, ESBL	Brownish yellow color indicating the presence of silver nanoparticles. The quantity of AgNO3 as the precursor affected the creation of Ag nanoparticles; a larger concentration of AgNO3 results in the production of additional particles.
Chang, C., Duan, B., Cai, J., & Zhang, L.	2010	ECH, Cellulose powder, aqueous NaOH/urea environment	Hydrogels in an aqueous NaOH/urea environment, swelling ratio was nearly 1000. Water retention of the hydrogels decreased 53% - 28% after 3 h of increasing CMC
Alam, M. N., Islam, M. S., Christopher, L. P.	2019	CMC, ECH, MCA, HCl, NaOH, C_2H_5OH,	Water retention reached 725 g d-water/g gel, and maximum WRV attained was 118 g s-water/g gel, weight ratio of CMC to ECH in the resulting hydrogels was kept at 0.75. Liquid holding ratio in industrial gels about 45 g/g.
Capanema, N. S. V., Mansur, A. A. P., de Jesus, A. C., Carvalho, et al	2018	Sodium carboxymethyl cellulose, Citric acid, PEG	Swelling degree about 4000%. FTIR spectrum of PEG the broad band in the 3700–3000 cm^{-1} region assigned to vO-H vibrations and the peaks at 3000–2800 cm^{-1} related to vC-H bands. For CMC, the major vibrational bands related to carboxylates (COO^-) asymmetric (1600 cm^{-1}) and symmetric (1416 cm^{-1} and 1324 cm^{-1})
G, R., C.R, R., Nair, S. V., & Menon, D.	2020	STMP, AlS crosslinker, Na-CMC, starch	The absorption of samples 2×2 cm^2 after applying a compressive load 50 g/cm^2 in saline solution.

Table 2.1: Comparison of Previous Studies "Table Contunied".

Gayet, J.-C., & Fortier, G.	1996	PEG, methylene blue, PBS	Water content BSA-PEG 8000 was 95.5%
B. Orhan, H. Kaygusuz, F. Bedia Erim	2022	Alginate, CMC, new quasi-cryogelation process, CaCl2, KH2PO4, NaOH, HCl,	Water absorption of 2343%, after five cycles it was 1200%, crosslinker content 3%, 5% $CaCl_2$, the swelling proportion of the beads was 1847% , 460%. The beads with 1:2 (Alg:CMC) and 2:1 swelled in isotonic solution 1082%, 750%. ratio of 1:1 which swelled 1847%. Alginate beads swelled 60% in pure water, 197% in isotonic solution, 90% in SGF, 1683% in SIF (at 90 min.) and 2066% in citrate-PBS (at 240 min.)
Batista, R. A., Espitia, P. J. P., Vergne, D. M. C.	2020	Chitosan, Alginate, FMC Biopolymer, Xanthan gum, Double distilled water	Chitosan has a strong influence on the maintenance of hydrogels structure, 3000% ratio in acidic fluid after 24 h. In acid environment reached 1665%, 2024%. At pH 7.0 it was 1005%, 667%. With swelling degree lower than 200% after 24 h. C1G2 180%, C1A2 136%. Highest swelling degree results were achieving 3046%. And C2A1 1592%. In FTIR-8300 spectrometer at 25 °C., were 4000-400 cm^{-1}. Sensitivity was 8 cm^{-1}.
Yan Hu, Tao Chen, Xiaoying Dong, Zhinan Mei	2015	SA, OSA, IPN,	Swelling ratio of the beads was 2300.
Yan H., Mengzhu z., x. Dong, Dan Z.	2015	Hyaluronic acid, Chitosan, Ca^{2+}/alginate	The swelling ratio of the beads at pH 7.4 was increased up to 120
Yan Hu, Jing Peng, Lei Ke, Dan Zhao, Haiyan Zhao & Xincai Xiao	2016	SA, CMCS, β-GP, SEM, IR and TG technique	Swelling rate of gel beads is 31.2 in 10.5h. At pH 1.2 the BSA discharged from the beads with release proportion 10%. whole releasing duration was raised to 11 h. at pH 7.4

Table 2.1: Comparison of Previous Studies “Table Contunied”.

Ting Guo, Ning Zhang, Jinbao Huang, Ying Pei, Fang Wang & Keyong Tang	2018	Glutaraldehyde, sodium alginate, water-soluble metformin hydrochloride, water-insoluble indomethacin	Proportion of storing reached 90% with a sodium alginate shell. The total breakdown of indomethacin was 8.7%.
Haniyeh M.j, Aleksey D. Drozdov, Jesper deC.	2023	Alginic acid sodium salt, $CaCl_2$, $SrCl_2$, $CuCl_2$, $ZnCl_2$, $FeCl_3$, HCl, deionized water	Iron has a stronger effect on the mechanical properties
Yue Z., Qiumin M., Faith C., P. Michael Davidson, Qixin Z.	2015	CBO, alginate films, SBO	SBO can enhance the antibacterial effectiveness and some properties of edible films. Film thickness 0.021-0.045 mm.

3. METHODOLOGY

3.1 MATERIALS AND METHODS

Alginic acid Sodium salt powder (Aldrich), Barium Chloride (Sigma-Aldrich), Cobalt Chloride (ISOLAB), Copper Chloride (Sigma-Aldrich), Nickel Chloride (Sigma-Aldrich), Calcium Chloride (Sigma-Aldrich), Iron Chloride (Sigma-Aldrich) and Cerium Chloride (Sigma-Aldrich).

A shaking water bath (Nüve ST-30), magnetic stirrer (Heidolph), precision balance (Ohaus) were used for daily labwork. All solutions were prepared with ultrapure water taken from the pure water device (Rephile- Direct Pure) device.

3.2 PREPARATION OF SODIUM ALGINATE SOLUTION

1 g of sodium alginate powder resulted by 50 mL, 2% Alg, a 50 mL of deionized water added to the powder of this Na-ALG in a beaker and a magnet was placed in the beaker and started to stir on stirring device with 170 speed for 30 minutes till comes pure solution without any particles and then left to use later for crosslinking.

3.3 CROSSLINKING PROCEDURE WITH CALCIUM CHLORIDE

After Na-Alg solution was prepared, a 0.2 mol/L was used to get a 2.94g of CaCl2, the weighed out Calcium Chloride was taken by precision sensitive scale and mixed with a little bit of deionized water to dissolve it, also a piece of magnet was used as a stirrer and put in magnetic stirrer device with 170 rpm and crosslinking process started by taking 10 ml of prepared alginate liquid by syringe dropped to the crosslinking solution that was about 20 cm height and stirring for approximately 20 minutes, and this procedure repeated again with another 10ml and 5ml. Then, the resulted hydrogel beads were carefully removed, washed twice to remove the accessing of calcium, and dried with a clean tissue before being placed on 3 different small plate and distributed them after that put aside in air to dry at room temperature for about 2 days are shown in the Figure 3.1. This procedure was repeated to Cobalt, Nickle, Iron, Cupper, Barium and Cerium.

Figure 3.1: Calcium Alginate Beads**.**

3.4 PREPARATION OF SWELLING SOLUTIONS

Swelling tests were carried out in Deionized water, Isotonic solution, SIF and SGF solutions.

3.4.1 Preparation of Isotonic Solution

0.9% (w/v) Sodium chloride which is 0.9g of NaCl powder was weighed and dissolved in 1L of deionized water and used for swelling for all the list of chemicals.

3.4.2 Preparation of Simulated Gastric Fluid

0.6g of NaCl2 was dissolved in 200ml and mixed, 2.1 ml of HCl was added to NaCl2 solution. Beaker and automatic pipette was used three times to adjust pH at 1.2 then completed the solvent to 300ml. Small amount of acid was added to beaker and acid put in NaCl gently after that completed to 100ml by using cylinder.

3.4.3 Preparation of Simulated Intestinal Fluid

Potassium dihydrogen phosphate was used and weighed to have a concentration of 0.05 mol/L. After dissolving with some deionized water, 7.7 mL of 0.2 mol/L NaOH was added and the volume was completed to 100 mL. The pH was adjusted to 6.8 with 0.2 mol/L NaOH or 0.2 mol/L HCl solution.

3.5 THE SWELLING TEST

we took each bead separately to make swelling test on it. The swelling degrees of the beads were measured gravimetrically. Swelling tests were performed in 20ml deionized water for 2 sample caps of Co, Ni, Ca, Fe, Cu, Ba and Ce beads, taken at 0.1 g and submerged into swelling solutions. Incubated beads were swollen in a water bath 37 C° 70 rpm shaking rate. The beads were filtered from their solution at specific time intervals for 4 hours like (15-15-30-30-30-60-60) minutes and take them out by these intervals, and the excess solution was gently removed using filter paper. Then, the beads were weighed and submerged back. The experiment was replicated two times for each type of bead. Percentage swelling was calculated according to the following equation:

$$\text{Swelling \% : } \frac{m_f - m_i}{m_i} \text{ x } 100 \qquad (3.1)$$

Where m_f and m_i define the mass of swollen bead and the mass of the dried bead, respectively

4. RESULTS

4.1 GRAPHS OF SWELLING EXPERIMENT

Comparative results of different types of beads swelled in pure water are shown in Table 4.1 and Figure 4.1.

Table 4.1: Swelling Data in Pure Water.

Time (min)	% Ni Average	% Ca Average	% Cu Average	% Fe Average	% Ba Average	% Ce Average	% Co Average
0	0	0	0	0	0	0	0
15	~0	18.80 ± 1.15	~0	2.37 ± 1.72	12.01 ± 5.79	17.47 ± 0.98	405.0 ± 3.1
30	~0	18.51 ± 0.05	~0	1.78	6.18	16.73 ± 2.24	709.1 ± 0.4
60	~0	14.29 ± 3.21	~0	1.63 ± 0.46	3.77	14.42 ± 0.21	1092.1 ± 1.5
90	~0	12.75 ± 7.28	~0	0.89 ± 0.65	5.74	12.04 ± 0.70	1241.4 ± 0.1
120	~0	11.49 ± 6.36	~0	0.99 ± 1.61	6.11	11.85 ± 1.96	1361.3 ± 2.1
180	~0	10.67 ± 5.21	~0	~0	4.97	9.68 ± 0.84	1524.0 ± 0.1
240	~0	10.36 ± 6.74	~0	~0	2.54	7.95 ± 2.38	1609.0 ± 4.0

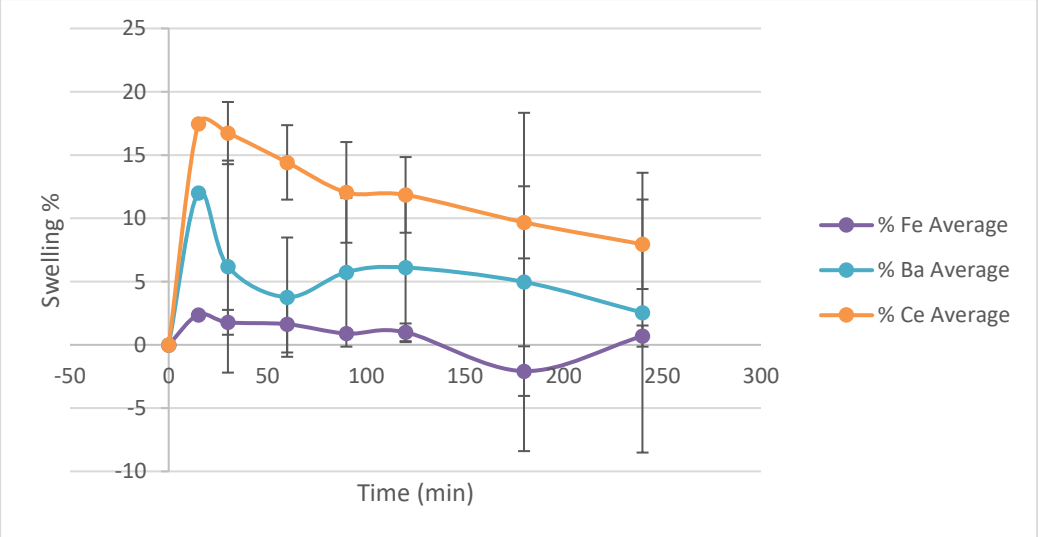

Figure 4.1: Comparative Swelling Graph in Pure Water.

As can be seen in Table 4.1 and Figure 4.1, nickel alginate and copper alginate beads did not exhibit any swelling in pure water. Iron, Barium alginate also does not have any swelling profile. Calcium alginate beads were swollen in pure water to a good extent. And Cerium was less than calcium.

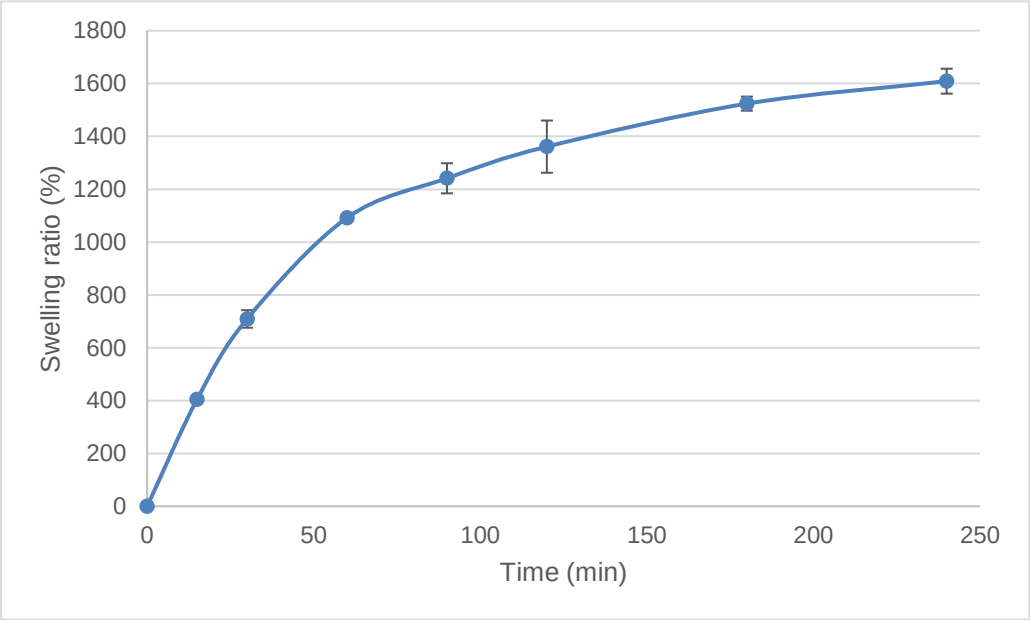

Figure 4.2: Swelling Graph of Cobalt Alginate in Pure Water.

The swelling profile of cobalt alginate beads was also plotted as it showed a large and regular increase profile. These swelling data fit the pseudo-second order kinetic profile very well by following the equation:

$$\frac{t}{Q_t} = \frac{1}{kQ_e^2} + \frac{t}{Q_e} \tag{4.1}$$

Where t is time in minutes, Q_t is the swelling ratio, Q_e is the swelling ratio at equilibrium, and k is constant. The data fits the classical pseudo-second order model with a R^2 value of 0.997.

Comparative results of different types of beads swollen in isotonic solution are shown in Table 4.2 and Figure 4.3.

Table 4.2: Swelling Data in Isotonic Solution.

Time (min)	% Ni Average	% Ca Average	% Cu Average	% Fe Average	% Ba Average	% Ce Average	% Co Average
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
15	15.86	22.29	29.95	26.61	54.09	-	170.4
30	12.46	39.90	27.61	26.71	64.02	-	543.4
60	9.51	73.02	21.94	23.32	88.96	-	979.6
90	11.19	101.1	24.88	21.15	118.5	-	1169.0
120	4.99	117.2	22.69	22.04	167.2	-	1267.4
180	5.52	128.6	22.34	18.99	146.2	-	1354.2
240	-	139.9	19.85	25.13	168.4	-	1376.6

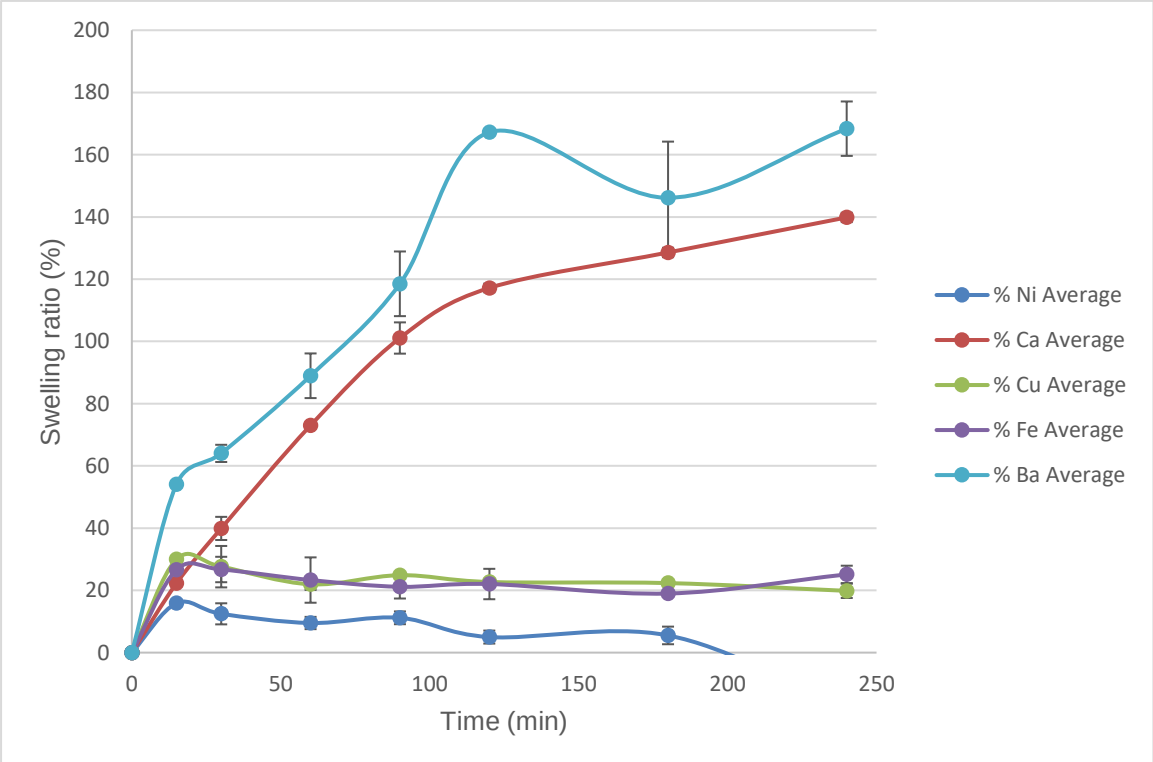

Figure 4.3: Comparative Swelling Graph in Isotonic Solution.

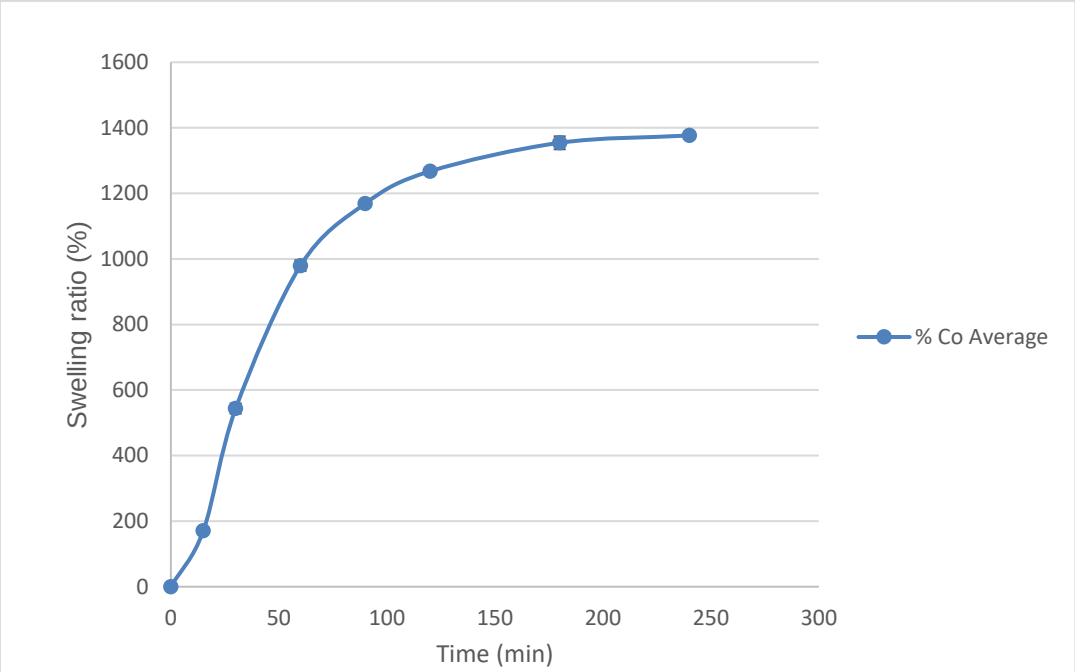

Figure 4.4: Swelling Graph of Cobalt alginate in Isotonic Solution.

Comparative results of different types of beads swollen in SIF are shown in Table 4.3 and Figure 4.5.

Table 4.3: Swelling Data in SIF.

Time (min)	% Ni Average	% Ca Average	% Cu Average	% Fe Average	% Ba Average	% Ce Average	% Co Average
0	0	0	0	0	0	0	0
15	94.32	16.50	46.36	47.78	24.60	32.23	222.7
30	672.4	42.25	42.17	29.14	24.70	32.04	1237.9
60	1928.9	134.1	39.12	20.54	37.47	49.25	2667.3
90	2565.3	260.6	39.23	20.88	87.47	62.71	-
120	2773.6	361.4	37.64	21.73	189.1	55.90	-
180	2890.2	463.8	41.32	20.58	410.9	-	-
240	2865.4	511.1	36.68	22.62	682.2	-	-

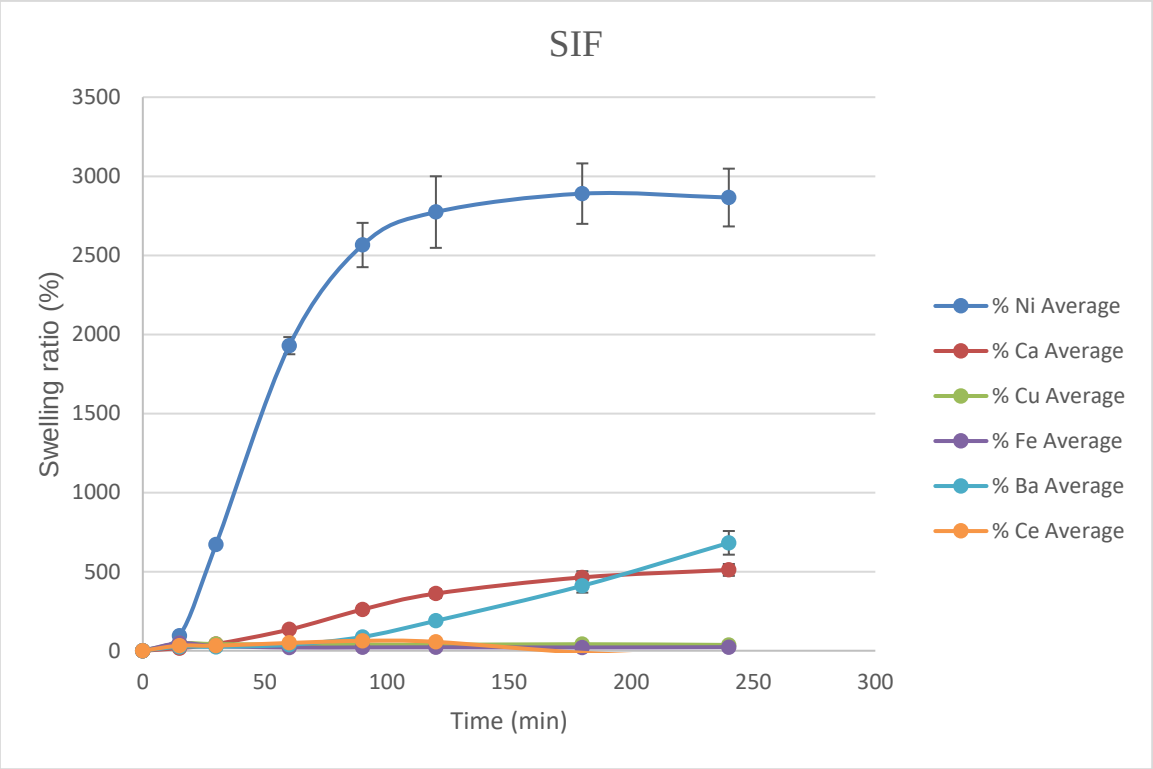

Figure 4.5: Comparative Swelling Graph in SIF.

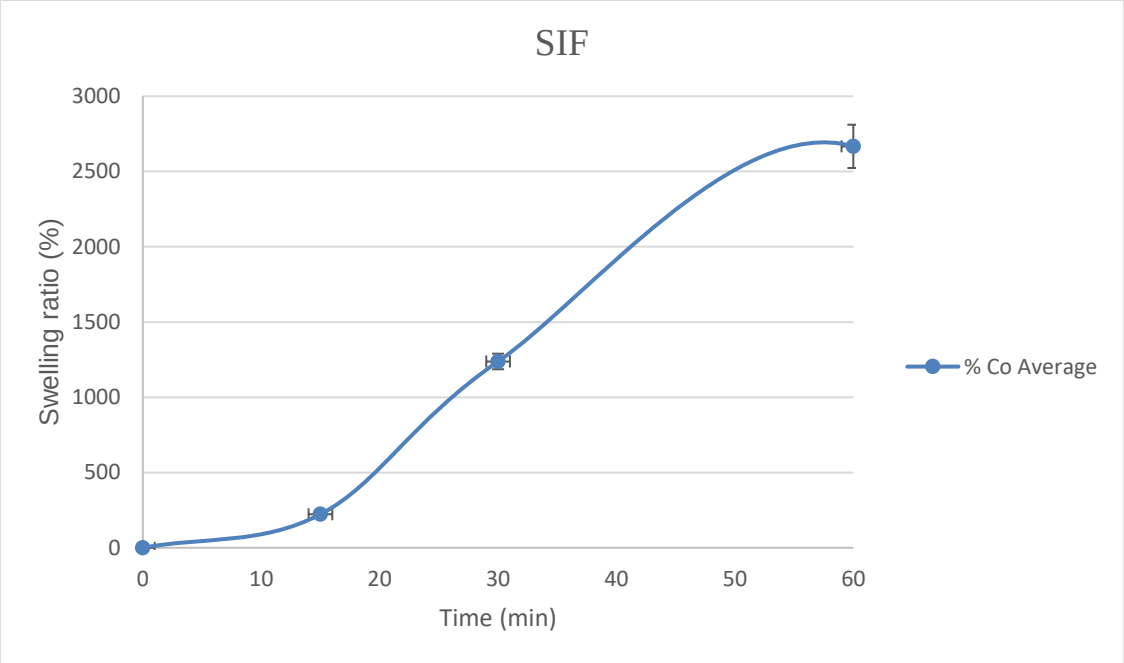

Figure 4.6: Swelling Graph of Cobalt Alginate in SIF.

Comparative results of different types of beads swelled in SGF are shown in Table 4.4 and Figure 4.7.

Table 4.4: Swelling Data in SGF.

Time (min)	% Ni Average	% Ca Average	% Cu Average	% Fe Average	% Ba Average	% Ce Average	% Co Average
0	0	0	0	0	0	0	0
15	86.23	25.86	53.52	29.04	11.01	13.55	87.15
30	73.56	17.54	49.57	25.20	16.19	2.58	69.77
60	68.72	16.80	22.36	18.92	30.64	-	70.07
90	67.37	16.00	19.77	24.00	32.04	-	69.82
120	63.92	14.72	17.03	23.75	29.20	-	63.94
180	64.52	13.47	19.77	24.95	29.25	-	65.54
240	61.68	13.77	18.72	25.35	28.00	-	68.58

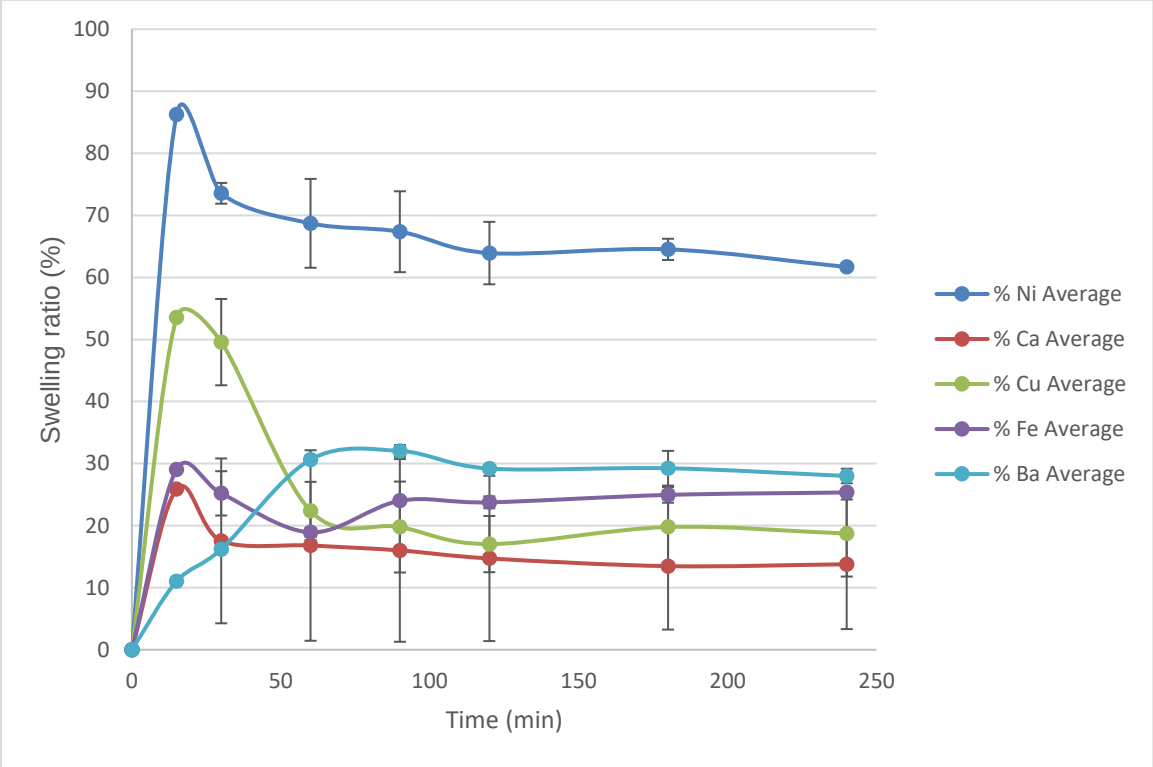

Figure 4.7: Comparative Swelling Graph in SGF.

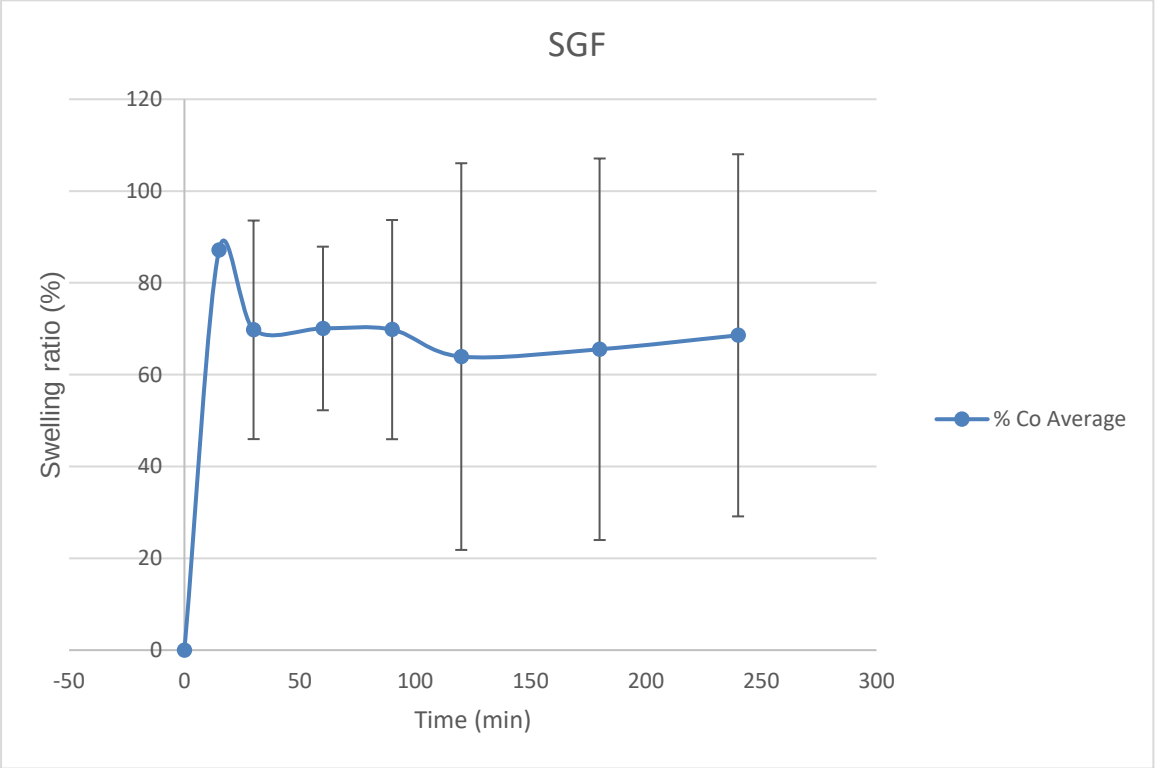

Figure 4.8: Swelling Graph of Cobalt Alginate in SGF.

In pure water, the swelling percentages of all beads increase, showing structural expanding and retention of water. Cobalt beads exhibit greatest expansion was about 1241% in 90 min because the permeable structure lets more water inside. Significant swelling appears in Calcium at 90 min about 12.7% but the Cerium was a little bit less than Ca. Nickel and Copper exhibit decreasing volume as seen by negative or minimal proportion changes refers to water absorption that restricted by higher crosslinking, network reduction, and ionic leakage. However, beads containing Fe and Ba crosslinking become more solid and have a lower potential for swelling as in Figure 4.1 and Table 4.1.

In isotonic solution, all beads have a slight rise in expansion at about 90 mins. Cobalt beads once more demonstrate large swelling approximately 1170% which is less than that of pure water. Calcium showed high swelling like 101% and 25% for the copper, that demonstrating enhanced absorption. But low swelling was seen in Ba, Fe, and Ni about 118%, 21%, and 11%. Also, it is important to note that Cerium occasionally displays reverse swelling values, which could indicate structural weakness or probable exchange of ions as in Table 4.2 and Figure 4.3.

In SIF, Ni showed huge swelling behavior and reached 2565% at 90 min. Compared to water and to isotonic medium, Cobalt swelled strongly 2667% at 60 minutes. Copper swelled in low amount about 39% and Calcium beads had significantly swelling to 260% at 90 min. Barium and Iron demonstrated steadily and controlled swelling 87%, 21%. This means that simulated intestinal fluid significantly increases swelling for Ni and Co crosslinked beads, indicating structural breakdown in acidic conditions. This solution possesses a fundamental acidity, so alginate beads especially these with lower ionic crosslinking are less stable. As in Table 4.3 and Figure 4.5.

Finally, in SGF conditions, between all previously mentioned solutions, cobalt beads display the least amount of swelling behavior which was around 70–100%. Also, Calcium and Copper showed very little swelling ~16–20%. And with comparing to SIF, Nickel exhibits significantly less fluid retention (~67%). Ba and Fe were steady with only a small amount of fluid retention for 24–32% that because of the strong polymer chains and increased durability in acidic conditions as in Table 4.4 and Figure 4.7.

4.2 FTIR RESULTS

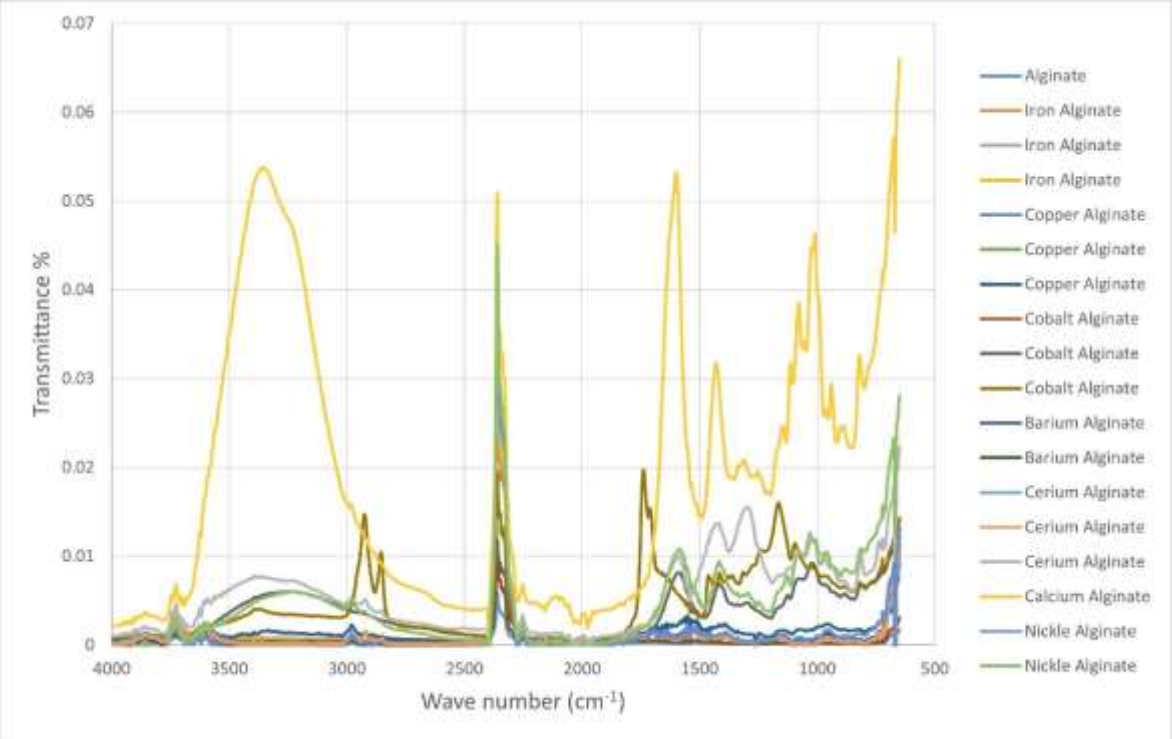

Figure 4.9: FTIR Spectra.

Results in Figure 4.9 show the FTIR spectra of the samples. Due to the mechanical properties of the beads, which are dry and small spherical materials, it was a challenge to measure the spectra correctly, and some spectra contains peaks from ambient impurities (such as carbon dioxide).

5. CONCLUSION

This study focused on the swelling of alginate biopolymer hydrogels crosslinked with different divalent and trivalent cations, which are nickel, calcium, copper, iron, barium, cerium and cobalt. In literature and industry, calcium alginate is widely used for various applications; however the use and research on other cations' interactions with alginate is relatively limited. Results show that different types of crosslinking cation may have varying effects on swelling behavior of the gels. Swelling is an important parameter in hydrogel applications since it regulates most characteristics such as diffusion of the molecules from the gel matrix. This property is critical in designing a proper drug delivery agent or adsorbent material. Main limitation of this study is the absence of molecular identification of the swelling behavior and electrostatic changes between crosslinker cation and alginate chain. Future studies might reveal these changes at molecular scale and the effects of molecular properties on macroscopic outcome, i.e., swelling.

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