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Utilizing κ-carrageenan Hydrogels in Teaching, Outreach and Chemical Gardens

Åbo Akademi
University

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PREFACE

The work presented in this thesis was carried out at the Laboratory of Molecular Science and Engineering, Åbo Akademi University during the years of 2019-2023 and in connection to upper secondary school visits to the Faculty of Science and Engineering at Åbo Akademi University during the spring of 2020.

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ABSTRACT

κ-carrageenan is a biopolymer that can be extracted from red seaweeds and has found great use for example in the food industry due to its excellent gelling, thickening and stabilizing abilities. The work done in this thesis investigates the utilization of κ-carrageenan in the growth of calcium phosphate chemical gardens with an educational touch. The term chemical gardens is used to describe the plant-like, seemingly growing, structures that result from the precipitation that occurs when placing crystal seeds of transition metal salts in silicate solution. Stemming from these classical chemical gardens a new multidisciplinary field termed *chemobrionics* has emerged. This is a field in which the research is focused on learning more about these structures, the processes behind them and how they can be controlled. While chemical gardens and chemobrionic structures in general continue to fascinate scientists, science itself does not seem to fascinate nor interest enough of young students today. Therefore, a future lack of STEM (science, technology, engineering, mathematics) professionals in all settings is a growing concern, nationally and globally.

The two main aims of the thesis were to investigate the use of κ-carrageenan hydrogels 1) as a base for developing teaching and outreach materials to offer teachers more available lab work, as these are usually appreciated by the students, and 2) as a replacement for the metal salt crystals usually used in chemical gardens in hope that hydrogels containing metal ions would give more control of the growth process. To make both the teaching material as well as the developed chemical gardens accessible for teachers to recreate at schools, a further, no less important, aim was to develop all processes so that they could be done utilizing food grade κ-carrageenan.

A writing board consisting of a κ-carrageenan hydrogel containing red cabbage juice was developed for the teaching of electrochemistry and for being used in outreach activities at the Faculty of Science and Engineering at Åbo Akademi University. The working principle of the writing board is based in the pH changes associated with the electrolysis of water. Additionally, two chemobrionic systems utilizing κ-carrageenan hydrogels for growing chemical gardens were created using teaching friendly materials and processes. Structures in the form of calcium phosphate tubes were grown from the interface of κ-carrageenan hydrogels containing either calcium ions (Ca-gel system) or phosphate ions (P-gel system). In both cases, the hydrogels were layered with a counterion solution (phosphate or calcium respectively). The effect of the time spent in the counterion solution (maturation time) on the created tubes was investigated in both systems. The effect of the amount of κ-carrageenan used in the hydrogels on the created tubes were investigated in the P-gel system.

The writing board concept as an outreach activity was evaluated by upper secondary school students visiting the Faculty of Science and Engineering at Åbo Akademi University, responding positively to the concept. Unfortunately, due to

the COVID-19 pandemic, only a trial version could be evaluated. A version aimed at classroom teaching was also developed but could not be evaluated for this same reason. Thus, no further development was done to either of the version.

The two chemical garden systems gave rise to tubes with observable differences in their macrostructure. Tubes grown in the Ca-gel system were straight and long while the tubes grown in the P-gel system were shorter and more kinked. The difference was partly explained by a larger pH difference between the hydrogel and the counterion solution observed in the Ca-gel system. For the P-gel system, increased amounts of κ-carrageenan in the hydrogel resulted in even shorter and thinner tubes. Analysis revealed that both systems resulted in more crystalline structures with increased time spent in the counterion solution, but the Ca-gel structures remained overall more amorphous. Further, tubes from both systems contained hydroxyapatite phases. Additional calcite phases were observed for the P-gel structures while the Ca-gel structures contained measurable traces of κ-carrageenan originating from the hydrogel. The chemical garden systems were developed with teaching and outreach in mind, but no trial or evaluation could be performed in this case either.

This work shows that κ-carrageenan can be used for creating teaching materials and as the seed containing one of the precipitating ions when growing chemical gardens. The work is adding to the knowledge of chemobrionic research by extending the library of (bio)polymers that can be used for growing chemical gardens. The relative ease, with which the hydrogel writing board could be prepared, makes the writing board as well as the red cabbage hydrogel a versatile lab work with potential use in many settings.

This work also contributes to the chemobrionic knowledge by showing that 1) tubular calcium phosphate structures can be grown from the interface of a κ-carrageenan-based hydrogel, 2) by introducing a chemical garden system where the anion (phosphate) is incorporated in the hydrogel phase of the system and 3) by showing that hydrogel systems can be inversed and thereby giving more new options for creating different kinds of structures. Additionally, it shows that hydrogel chemical gardens and materials research can be conducted while having teaching and outreach in mind during the whole process.

SAMMANFATTNING

κ-karragenan är en biopolymer som kan utvinnas ur rödalger och som har en bred användnings till exempel inom livsmedelsindustrin tack vare sina utmärkta egenskaper bland annat som förtjocknings- och bindemedel. I den här avhandlingen undersöks utnyttjandet av κ-karragenan vid skapandet av kemiska trädgårdar bestående av kalciumfosfat på ett sådant sätt att även undervisningsrelaterade aspekter hålls i åtanke. Termen kemiska trädgårdar används som beteckning för att beskriva de växtliknande strukturer som uppstår till följd av fällningsreaktioner när kristaller av övergångsmetallsalter placeras i en silikatlösning. Med dessa klassiska kemiska trädgårdar som utgångspunkt har ett nytt tvärvetenskapligt vetenskapsområde med namnet *kemobrionik* (chemobrionics) uppstått. Forskningen inom området fokuserar på att lära sig mera om dessa strukturer, hur de uppstår och hur de kan kontrolleras. Samtidigt som de kemiska trädgårdarna och övriga liknande strukturer fortsätter att fascinera forskare runt om i världen så verkar naturvetenskapen själv fascinera unga allt mindre. En framtida brist på expertis inom de naturvetenskapliga och tekniska områdena är därför ett orosmoment så väl nationellt som globalt.

De två huvudmålen med avhandlingen var att undersöka huruvida det är möjligt att använda hydrogeler baserade på κ-karragenan 1) som en utgångspunkt för att skapa material ämnat för laborationsundervisning och utåtriktad verksamhet riktad till skolor (outreach) och 2) för att ersätta kristallerna av metallsalter i kemiska trädgårdar med hydrogeler fyllda av metallsalt. Laborationsarbeten är ofta uppskattade av elever och att erbjuda lärare fler tillgängliga laborationsarbeten kunde öka på intresset för kemi. Genom att ersätta saltkristaller med saltfyllda hydrogeler kan man få mer kontroll över tillväxtprocessen av de kemiska trädgårdarna. För att göra det möjligt för vilken lärare som helst att ta in undervisningsmaterialet och de kemiska trädgårdarna i sin egen undervisning var ytterligare ett viktigt mål att allt kunde skapas med hjälp av κ-karragenan ämnat för matlagning.

En skrivplatta baserad på en κ-karragenanhydrogel innehållande rödkålssaft utvecklades för undervisning i elektrokemi och med tanke på att användas vid skolbesök till Fakulteten för naturvetenskaper och teknik vid Åbo Akademi. Skrivplattans funktionsprincip baserar sig på den pH förändring som sker vid elektrolys av vatten. Därtill skapades två kemobrioniska system innehållande κ-karragenanhydrogeler ur vilka det gick att odla kemiska trädgårdar genom att använda material och metoder som lämpar sig för undervisning. Kalciumfosfatstrukturer i form av tuber odlades från gränsytan av κ-karragenanhydrogeler innehållande antingen kalciumjoner (Ca-gel-systemet) eller fosfatjoner (P-gel-systemet). I båda fallen täcktes hydrogelerna med en lösning innehållande en motjon (fosfat respektive kalcium). Hur längden av den tid som strukturerna befann sig i motjonslösningen påverkade strukturerna

undersöktes i båda systemen. P-gel-systemet undersöktes också med avseende på hut mängden κ-karragenan i hydrogelen påverkade strukturerna.

Skrivplattan som aktivitet ämnad för skolbesök utvärderades av gymnasielever som besökte Fakulteten för naturvetenskaper och teknik vid Åbo Akademi. Mottagandet av konceptet var positivt. Dessvärre kunde endast en testversion av skrivplattan utvärderas eftersom Covid-19 pandemin satte stopp för ytterligare elevdeltagande. En version av laborationsarbetet med skrivplattan ämnad för klassrumsundervisning utvecklades men kunde således inte heller utvärderas. På grund av detta utfördes inte någon fortsatt utveckling av laborationen i någondera formen.

De två systemen utvecklade för kemiska trädgårdar gav upphov till strukturer med märkbara skillnader i makrostruktur. Tuberna i Ca-gel-systemet var raka och långa medan tuberna i P-gel-systemet var kortare och krokigare. En delorsak till strukturen kunde förklaras av den betydligt större skillnaden i pH mellan hydrogelen och motjonslösningen i Ca-gel-systemet. Inom P-gel-systemet kunde man erhålla kortare och tunnare tuber genom att öka mängden κ-karragenan i hydrogelen. Analys av tuberna visade att båda systemen gav upphov till mer kristallina strukturer ju längre tid de befann sig i motjonslösningen, men att tuberna i Ca-gel-systemet överlag förblev mer amorfa i jämförsele med de från P-gel-systemet. Från båda systemen erhölls tuber med hydroxiapatitfaser. Dessutom innehöll P-gel-tuberna kalcit medan Ca-gel-tuberna innehöll små men mätbara mängder av κ-karragenan med ursprung från hydrogelen. Systemen med de kemiska trädgårdarna utvecklades med undervisning och skolbesök i åtanke, men varken tester eller utvärderingar kunde utföras i det fallet heller.

Detta arbete visar att κ-karragenan kan användas både i undervisning och för att ersätta kristaller av metallsalt vid skapandet av kemiska trädgårdar. Därmed bidrar detta arbete med att utöka listan av (bio)polymerer som kan användas för att tillverka hydrogeler i kemobrioniska system. Då skrivplattan kunde framställas relativt lätt har både den och rödkålshydrogelen potential att användas i flertalet sammanhang och med olika typer av grupper.

Detta arbete bidrar också med ökad kunskap inom forskningen av kemobrionik genom att visa att 1) tubulära kalciumfosfat strukturer kan odlas från gränsytan av en κ-karragenanhydrogel, 2) genom att introducera ett system där anjonen (fosfat) ingår i hydrogelfasen av systemet och 3) genom att visa att hydrogelsystem kan inverteras vilket därigenom ger nya möjligheter att framställa flera typer av strukturer. Arbetet visar därtill att kemiska trädgårdar odlade utifrån hydrogeler samt materialforskning kan utföras med undervisning och outreach i åtanke under hela processen.

LIST OF ORIGINAL PUBLICATIONS

The thesis is based on the following original publications, referred to in the text by their Roman numerals I-III:

I. **Fogde, A.**; Kurtén, B.; Sandberg, T.; Huynh, T.-P. Colorimetric Hydrogel from Natural Indicators: A Tool for Electrochemistry Education. *Journal of Chemical Education.* 2020, 97 (10), 3702–3706.

II. **Fogde, A.**; Qudsia, S.; Le, T.-A.; Sandberg, T.; Huynh, T.-P. (Calcium-Phosphate)/Carrageenan Gardens Grown from the Gel/Liquid Interface. *ChemSystemsChem*, 2021, 3 (4), e200006

III. **Fogde, A.**; Rosqvist, E.; Le, T.-A.; Smått, J.-H.; Sandberg, T.; Huynh, T.-P. A Further Study on Calcium Phosphate Gardens Grown from the Interface of κ-Carrageenan-based Hydrogels and Counterion Solutions. *ChemPlusChem* 2023*,* 88*,* e202200426

SUPPORTING MATERIAL

1. The Table and the Tubes – exhibition booklet by J-E Andersson, T.-P. Huynh, **A. Fogde**. Printed version presented alongside exhibition of the "The Table and the Tubes" art piece at Lilla Fabbes, Turku (autumn 2021 and spring 2022), Söderlångvik gård, Dragsfjärd (summer 2022) and Aboa Vetus Ars Nova, Turku (spring 2023).

CONTRIBUTION OF THE AUTHOR

(I) Fogde was responsible for ideating and developing the concept, planning and performing the experimental work and evaluation, analysis of the results and writing the first draft of the article. Fogde was the main writer of the paper. All authors contributed to the reviewing and editing process of the manuscript.

(II) Fogde was responsible for planning and performing the experimental work, analysis of the results and writing the first draft of the article with the following exceptions: SEM/EDS measurements were performed by M.Sc. Linus Silvander, TGA measurements were performed by Le and part of the analysis was done by Le and Huynh. XRD measurements were performed by Qudsia. Fogde was the main writer of the paper. All authors contributed to the reviewing and editing process of the manuscript.

(III) Fogde was responsible for planning and performing the experimental work, analysis of the results and writing the first draft of the article with the following exceptions: SEM/EDS measurements were performed by M.Sc. Linus Silvander, TGA and XRD measurements were performed by Le, AFM measurements and analysis were performed by Rosqvist. Fogde was the main writer of the paper. All authors contributed to the reviewing and editing process of the manuscript.

ABBREVIATIONS

β-TCP	β-tricalcium phosphate
ACP	Amorphous calcium phosphate
AFM	Atomic force microscopy
Ca-gel	Chemobrionic system with calcium ions in the hydrogel
CaP	Calcium phosphate
CDHA	Calcium deficient hydroxyapatite
CO_3A	Carbonated apatite
DCPD	Dicalcium phosphate dihydrate
EDS	Energy dispersive X-ray spectroscopy
FT-IR	Fourier transformed infrared
HA	Hydroxyapatite
P-gel	Chemobrionic system with phosphate ions in the hydrogel
RSC	Royal Society of Chemistry
SDD-EDS	Silicon drift detector energy dispersive X-ray spectroscopy
SEM	Scanning electron microscopy
STEM	Science, technology, engineering, mathematics
TGA	Thermogravimetric analysis
XRD	X-ray diffraction
ÅAU	Åbo Akademi University

1. INTRODUCTION

I am sure you are familiar with gardens, but what is a chemical garden? Do you know what hydrogels are? Have you heard about κ-carrageenan? Perhaps unknowingly you might be acquainted with most of them, maybe even all. The word carrageenan is likely familiar to those having the habit of looking through the list of ingredients on groceries when shopping while hydrogels are found in everyday products such as contact lenses, diapers and toothpaste.[1,2] Carrageenans are a family of polysaccharides that can be extracted from red seaweeds.[2,3] There are different types and kappa (κ)-carrageenan is one of the commercially most important ones.[2] The carrageenans have excellent gelling, thickening and stabilizing abilities and are therefore widely used, for example in the already mentioned food industry.[2–5] They can also be used for making hydrogels: three-dimensional networks able to hold large amounts of water.[6] In addition to many common items hydrogels are also important, for example in applications within biomedicine, sensing, drug delivery and wastewater treatment.[6,7] Hydrogels are very versatile as they can be made from a variety of polymers that can be natural (e.g., carrageenan) or synthetic (e.g., poly(vinyl alcohol)), are simple to prepare and have both tunable properties and functionalities.[6,8] Hydrogels based on carrageenans are thermo-reversible with textures ranging from soft and elastic to brittle and firm.[5]

Now if you are lucky, you might also have had the pleasure of admiring chemical gardens in your chemistry classroom. The structures of the chemical gardens can be grown from colorful salts such as cobalt(II) chloride (dark blue), iron(III) chloride (yellow) and nickel(II) chloride (light green), thus making them an excellent example of the beauty of chemistry and thereby a popular demonstration in the chemistry classroom but also in chemistry sets intended for children.[9–11] The term chemical garden is used for the hollow structures formed when a soluble metal salt, often in the form of a seed crystal, is placed in an aqueous solution of an anion, typically silicate (SiO_3^{2-}).[9,12–14] Upon forming, the structures are seemingly growing upwards and the resulting structures resembles those of a plant.[15] The actual formation of the gardens revolves around a precipitation reaction in which a semipermeable colloidal membrane is formed and across this membrane, osmosis will occur.[15,16] Water will be drawn through the membrane; the salt seed will continue to dissolve, and the membrane will stretch for as long as it can.[15,16] Eventually the membrane will rupture and a jet of the fluid from inside the membrane will be ejected into the surrounding solution, forming a tube of precipitate as the two solutions meet.[15,16] This newly formed precipitation membrane will allow for the process to continue in cycles for as long as the conditions are right.[15,16]

Why the current interest in these structures and these processes? Well, the chemical gardens have fascinated many scientists since they were first described in the 17th century.[17,18] Today's knowledge and the importance of these chemical garden systems reach far beyond the early experiments and the mere beauty of the structures.[16,17] From the basis of the chemical gardens systems with their semipermeable membranes, a new field termed "Chemobrionics" has emerged.[17–19] The term stems from the words "chemo" and the Greek word "bruien", meaning to grow or to enlarge.[19] Within the field of chemobrionics this growing refers to the growing owing to osmotic pressure.[19] The field of chemobrionics intersects with materials science, chemistry, physics and biology, and studies self-organizing biomimetic precipitation structures that involve semipermeable membranes, but also amorphous and polycrystalline solids.[19] At the moment the chemobrionic research is still very much revolving around fundamental scientific research, where challenges such as optimization of the tubular structures and controlling their morphology, thickness and size remain to be solved.[19] Yet, among the already developing applications things such as hard-tissue engineering[20], biochemical delivery[21], fuel cells[22,23], microfluidics[24] and chemical motors[25–27] can be mentioned. Hopes are also up that the chemobrionic research will give more insight into the origin of life, more precisely regarding the theory that life began at the hydrothermal vents on the ocean floor.[17,19,28] Additionally, further research into chemobrionics are expected to contribute to application within topics such as hydration of Portland cement, catalysis, adsorption, filtration and sensors.[19] The chemobrionic structures can be grown in many ways, for example using the already mentioned seed growth, via injection or even from the surface of a gel as we will see also in this thesis.[15,17]

The need for new and improved materials is constant as we stand before many challenges, such as environmental issues, that will require new methods and materials to be solved. However, the ability to solve these challenges is very dependent on a constant growth of new generations of scientist. At the same time, it is just as important for everyone, also those choosing a completely different (academic) path, to have some knowledge of chemistry and sciences in their everyday life. Some will need it in the important roles of decision makers, but everyone will need it for making environmentally friendly decisions as consumers and as members of an increasingly technological society. Therefore, it is of uttermost importance that we can offer high-quality teaching and inspiring outreach activities to children and adolescents. Research shows that both the teacher and the actual teaching have a high impact on the future interest and attitudes towards science among students.[29–32] But the students meet chemistry in a learning context also in other places. For instance, it has been shown that outreach activities and learning outside the classroom can also be utilized to increase interest and positive attitudes.[33–35]

This thesis offers an introductory exploration into the fascinating world of some of the chemistry that can be done with household materials through electrochemistry teaching and chemical gardens. Via the investigation of pH changes and tubular structures grown at the interface of hydrogels based on κ-carrageenan. There is reason for all scientists to communicate their science and taking part in inspiring students to pursue careers in science, technology, engineering and mathematics (STEM) as well as raising interest in science. Therefore, throughout the process of tis work, the thought of making all experiments accessible also to school students has always been present. As a result, the materials developed in this thesis can be used both for outreach purposes and for the teaching.

Why did I decide on this topic, this approach? The short answer is because chemical gardens are so very fascinating and because I love teaching. The world of chemistry, filled with exiting phenomena, never ceases to amaze me. My motto as a science teacher has always been “science for all”, instead of “science for some”. In addition to science education, the field of science communication also lies very close to my heart. Therefore, doing my very best in making the fascinating worlds of hydrogels and chemical gardens accessible to all was a very important aspect of my work.

1.1. Objectives

The main objective for this thesis was to investigate the possibility of using the biopolymer κ-carrageenan for creating hydrogels suitable for developing teaching materials and as a basis for exploring new kinds of chemical garden systems suitable for growing chemical gardens. The teaching material as well as the chemical garden systems and their manufacturing processes were aimed to be made suitable for both teaching and outreach. The initial objective for all studies was to formulate the right conditions of the hydrogel to allow its use for the intended purposes.

The objectives for the development of teaching materials were to offer an engaging yet safe platform dealing either with a core subject of chemistry or with a subject that is known to be challenging for students, preferably both (**Paper I**). The aim was to develop a platform with as wide use as possible. Therefore, the target groups were lower (grade 7–9, 13–15-year-old students) and upper secondary school (grade 10–12, 16–19-year-old students) students and was not specified beyond this. Further, the platform should be easy for teachers to manufacture and scale to their needs.

The main objective for the studies of chemical gardens were to create a system that allowed chemical gardens structures to grow from the gel/liquid interface. This was successfully accomplished for two kinds of systems: a basic system and an inverted system (**Paper II**). Further objectives were to investigate the systems, the properties of the grown structures and if they could be controlled through the properties of the hydrogel (**Paper II**) and finally, to compare the possible differences between the two obtained systems and their structures (**Paper II**, **Paper III**).

1.2. Research approach

The approach towards all the lab work done in this thesis was always to create methods that could easily be used and repeated in classroom settings, but without compromising on the quality of the obtained results. The approach for the developed teaching material was to create methods that could be reproduced even in the kitchen at home using materials that could be obtained by anyone from the grocery or hardware store. Hence, food grade κ-carrageenan has been used throughout this thesis. For the same reasons only basic lab ware has been used for preparing solutions and hydrogels, as well as in the creation of the chemical garden systems. The assessment of the development of the teaching concepts, were meant to be done through initial testing with a small group of students where feedback would be gathered. Based on the feedback the concepts would be revised (if need be), before trying them with a larger set of students.

The approach for the chemical gardens was to successfully create a functional system at the interface of a κ-carrageenan hydrogel and an aqueous salt solution. Thereafter the approach was to learn more about this system and its dependence on the κ-carrageenan and the location of the ions participating in the precipitation process, rather than focusing on optimizing the system to its full potential via a larger set of parameters.

Calcium phosphates (CaPs) were chosen as the chemical garden models to be investigated, as they are more environmentally friendly than many other alternatives such as those based on heavy metals. In addition, CaP structures had been grown by others at the gel/liquid interface, and comparisons with other hydrogel systems could be done. However, the works of others had all been based on systems with the calcium ions incorporated into the hydrogel. Therefore, this work began by trying to create a functional chemical garden system where the phosphate ion was incorporated into the hydrogel. This approach had not been presented previously. To put the developed systems and the obtained structure into perspective, a system with the calcium ion in the hydrogel was also developed to allow comparison with structures previously reported by others. Chemical garden systems of both these kinds were successfully obtained. To bring forward the investigation of the structures of the phosphate hydrogel system better, much of the investigation into the developed systems were done as a comparison between the two. Investigations were focused of the properties of the systems and the obtained chemical garden structures.

1.3. Contribution of this work

The teaching material developed within this work contributes with a versatile and engaging platform for teaching electrochemistry and acid-base reactions. The developed platform can be used as a demonstration but more importantly also by the students themselves. Additionally, it can be used for outreach activities. The material can easily be manufactured by the teacher from readily available materials, is safe to use for the students and, additionally, demonstrates everyday chemistry. Further, the developed platform contributes with a bilberry (blueberry) based pH indicator experiment in addition to the red cabbage experiments that are more often used in teaching.

To the best of our knowledge, no work had previously been done where chemical garden structures (especially CaPs) has been grown from the interface of a κ-carrageenan-based hydrogel. But more importantly, this is the first work in CaP chemical gardens where phosphate ions have been used in the hydrogel part. Thereby, this work contributes with important knowledge to the current state-of-the-art regarding chemical gardens grown from gel/liquid interfaces. Not only does this work provide information about a new type of gel/liquid interface, but it also provides novel insight into the possibilities of inverting the positions of the ions in the gel/liquid-system and how this can affect the properties of the structures. Furthermore, this work contributes to the dissemination of the topic as the work has been developed with outreach in minds and has additionally been exhibited as part of the project "Forcing the Impossible – Avtryck i det okända"[36,37], a project where science meets art. A glimpse of this can be seen in the exhibition booklet found in the Supporting Material (SM1).

2. BACKGROUND

This thesis has two main themes: 1) teaching and outreach and 2) chemical gardens. This section will focus on four topics that are relevant to the work presented later. The aim of STEM outreach is often to increase interest in STEM among those taking part in events. The outreach theme is present in all parts of the thesis, and we will therefore start by taking an overall look at interest in STEM among students and how outreach can be utilized. A second common factor for all the articles presented is the use of hydrogels and so the second part of this section is dedicated to this topic. The next part is dedicated to chemical gardens, followed by a part on CaPs to give some background to the chemical garden structures obtained within this particular work.

2.1. Students as a future scientist?

A decreasing interest for science among students has sparked a discussion that has been going on for decades, and is unfortunately still relevant today.[35,38,39] Concern has been raised due to an expected continued increase in the need for trained professionals in the STEM domain.[40–46] From a Finnish perspective a future lack of science teachers is as also a critical issue and a decrease in students can already be seen.[47] A lack of trained professionals in science education will eventually affect knowledge and competitiveness in many fields.[38,47,48] However, as the role of science and technology expands in our everyday lives this is an issue that touches upon us all.[49,50] Many countries are therefore also concerned with the declining knowledge in the STEM subjects.[39,51–53] Knowledge in these subjects is an important part of general education both for individuals as such and for them as members of society; science is present in news topics, daily decisions and applications but is also important for responsible and active participation in a society relying on technology and research.[46,54–57] This is also reflected in the Finnish curricula. The curriculum for lower secondary school states that the teaching of chemistry should support the pupils understanding of chemistry and the roles it plays in daily life and society, as well as for a sustainable future.[58,59] The curriculum for upper secondary school highlights aspects such as the importance of chemistry and its applications for solving environmental issues and how the teaching should support the student in critical evaluation of daily decisions and public discussions.[60,61]

2.1.1. Students' interest in science and chemistry

A lot of effort has been put into the research of both interest and attitudes within the field of science education.[50] In the public debate the use of the term *interest in science* is mostly used to describe the number of students choosing to pursue a career in STEM.[39,56] In science education it is often seen as describing the interest in the subject itself, but a lack of consensus in the field as to what exactly is measured and referred to is acknowledged (e.g., achievement, attainment, attitudes).[62,63] Yet interest can be described as something content specific that emerges from the interaction between an individual and something specific (e.g., a topic) in their environment and can last for longer or shorter periods.[64,65] The concept of "attitudes toward science" is also used often and can be described as feelings, values and beliefs held about objects related to science, such as scientists, school science or the impact of science.[38] Interest and attitudes are both important, since the former can affect the latter and both can affect learning.[38,66–68]. The focus here will be on interest.

Interest as such can be divided into personal (or individual) and situational interest.[64,66] The personal interest is longer-lasting, develops over time and tends to be more stable, thus having longer lasting effects on an individual's values and knowledge.[64,66] The situational interest is context specific as it is externally triggered by something in the environment, usually last for shorter periods and tends to have only a short-term effect on values and knowledge. [64,66] However, it is argued that the situational interest can be utilized to encourage students' involvement in learning of specific content and that it can eventually develop into the longer-lasting individual interest.[50,64,69] Interest and attitudes towards science are laid already in early childhood.[49,50,70] However, a decline in the interest and attitudes towards science can be seen beginning from the age of 11.[71] This can accelerate from the age of 14 onwards, and be seen especially in the transmission between elementary and secondary education.[38,67,71,72] Unfortunately it seems to be very hard to gain interest once it has been lost, making positive experiences of science and its teaching all the more important starting all the way from primary school.[49,71,73]

Why do students lose their interest? Research has offered explanation such as content that is decontextualized and seen as irrelevant or boring, perceived difficulty of school science, teaching strategies (such as transmissive pedagogy or excluding teaching), lack of creativity, expectations on science that are not met in the teaching situations or by the content, overloaded curricula and home background.[30,38,57,63,73–76] Some also argue that the big issue isn't that interest is lost but rather that it never developed.[62,77] Many similarities can be found when looking more closely at the interest in chemistry alone: lack of relevance, difficulty (e.g., with models used in chemistry education) and curriculum overload for both context-bases as well as more conventional courses.[78]

An important aspect in the discussion is, however, that even though many lack interest in science classes, or so-called *school science*, they still show interest in science and see it useful in both everyday life and for future work.[56,79] The majority of students also recognize the importance of science, but they just don't see it as something for themselves and would rather let others deal with it.[48,75,80–83] Many students simply find other subjects more interesting, and even though students might be interested in science, they still do not find interest in pursuing a career in STEM.[73,81,84] The interest in a STEM career is, however, a difficult issue as it is also affected by multiple other factors such as representation, ethnicity, socio-economic background, friends and parents.[70,81,85]

Making changes in the classroom is not the only way to deal with the problem. Non-formal education can also play its part in increasing interest. The materials and methods developed in this thesis aims at introducing new activities for outreach and teaching, rather than making any changes to how science is taught. In the current context, outreach should be seen as activities aiming to inspire in the form of non-formal science education such as workshops, experimental settings and science shows. Non-formal learning can be said to occur in a planned (but flexible) manner for example by organizations or institutions and is offered at places such as scientific centers as well as science clubs and camps.[86] In Finland non-formal education is for example arranged in the form of science birthday parties, clubs and camps.[87–92] Many of these are organized by LUMA Centre Finland and they have shown to increase interest in science among the attendees.[33,93] In addition, many of the Finnish universities also offer outreach activities in the form of school visits to campus and different laboratory spaces.[94–96]

When working with outreach, one of the key aspects is defining your intended audience and strategies.[97,98] At Åbo Akademi University (ÅAU) the outreach done by the Faculty of Science and Engineering is primarily directed towards upper secondary school, often in the form of visits to the university campus. We will therefore look a bit closer on activities intended for students in similar ages. Outreach can be done for several reason such as disseminating science, to inspire, to teach or to recruit.[99–103] Some examples of activities offered at other universities are laboratory visits, shadowing a researcher, lectures and demonstrations, summer and apprenticeships programs, different kinds of activity days and science camps.[95,104–114] The implementation varies from short and simple visits to or from campus to more thorough programs that include both pre- and post-materials for the students and might also be divided over several days.[107,108,115,116]

Just as with other outreach, chemistry outreach also has several aims. Sometimes the main aim is to teach, such as is often the case of the outreach done by the American Chemical Society via college students, and at other times the main aim is to inspire.[103,117,118] But as the final career decision in upper secondary school fluctuates, well implemented outreach activities also have the opportunity to influence the career choice among those who still regard STEM as an option.[119–122] Studies show that activities that span over longer time have a higher chance of influencing, compared to single interventions.[102,107,120,123,124] A couple of the things that seem to enhance interest in a STEM career is the real-world relevance of STEM and the opportunity to take part in actual research.[111,125–127] Additionally, these can also enhance interest and learning.[107,108] An important aspect of many successful initiatives on campus is also the opportunity to meet role models in the form of staff and undergraduate students. This is especially important for underrepresented groups.[85,97,107,123]

However, these longer initiatives are not always possible to arrange and it has also been shown that targeted recruitment initiatives in the form of university websites and visits, especially the ones to campus, can inspire some near their educational decision points.[128] A lot of chemistry outreach is often done via hands-on experiments or demonstrations of experiments, with intended audiences ranging from children to adults.[118,129,130] Sometimes the focus is just on basic chemistry, such is often the case with children and especially younger ones.[131,132] But many laboratories also offer activities based on their own specific field or research area.[133–137] Examples of outreach activities in chemistry that have gathered positive response, also regarding future career aspirations, are reverse science fairs, laboratory experiments during science festivals and interactive lectures.[123,138,139] Important factors of campus outreach in chemistry is the opportunity to take part in hand-on exercises. [99] In fact, experiments that cannot be conducted at school are often popular also among participating teachers.[99] Other important factors for successful outreach initiatives are that they are well planned, implemented properly and that necessary support, guidance and training is given to those involved.[107,123,124,140,141] Proper training helps with avoiding misconceptions and misunderstandings of both the taught concepts as well as beliefs regarding teaching and learning among those arranging the outreach activity. These misconceptions and misunderstandings are unfortunately common also among science majors doing outreach.[117,142]

Finally, what makes someone choose to study chemistry? One of the main reason for enrolling in a chemistry program is for many the interest and enjoyment in the subject.[143] These reasons can also be found among Finnish chemistry students at university as well as reasons for upper secondary school students to choose elective chemistry courses.[144–146] The positive impact of campus visits or other exposition to educational institutions was seen in both a Finnish and a Norwegian study.[128,146] Studies in several countries show that many students in upper secondary choose science courses due to future career aspirations, even though they are not necessarily aiming at a STEM career.[75,147–151] STEM outreach at Finnish universities could therefore very well be aimed both at teaching and at inspiring to a career in science. Students seem to be more interested in content of today, rather than people in the past and what is already known.[57] Which is in line with including contemporary research in activities. Further, students in Swedish studies listed more connections to everyday life, laboratory work, educational visits among their improvement suggestions for their upper secondary chemistry education.[78,151] This, together with the fact that visiting a university laboratory can affect interest, can very well be used to one's advantage in outreach settings by providing more laboratory exercises.[140]

2.2. Hydrogels

A gel is defined as a "non-fluid colloidal network or polymer network that is expanded throughout its whole volume by a fluid" (IUPAC recommendations 2007).[152] In the case of a hydrogel this fluid consists of an aqueous medium and for the individual polymer chains to be able to absorb water they need some degree of hydrophilicity, often provided by groups such as -SO_3H, -NH_2, -COOH and -OH.[7,152–154] Osmotic pressure and capillary effect also aids in the networks ability to absorb water.[7] The disintegration of the hydrogel is prevented by the cross-linking of the network, which prevents the polymer chains from dissolving.[6,7]

Structurally, hydrogels are made up of a network of polymer chains arranged into a mesh-like structure, where the polymer chains are networked either by physical interactions or covalently by using a cross-linker.[6] Based on the nature of the crosslinking, hydrogels can be divided into chemical hydrogels and physical hydrogels. The chemical and covalent crosslinking causes configurational changes, making the hydrogel irreversible and permanent. The physical hydrogels on the other hand are reversible as their crosslinking is achieved by physical processes such as hydrogen bonding, hydrophobic association and ionic interaction that only give rise to conformational changes. This gives the physical hydrogels advantages such as biodegradation, reshaping and non-toxicity.[7,153] The preparation and gelation processes vary with the type of polymer and crosslinking used. Chemically crosslinked gels can for example be prepared through chemical crosslinking, radical polymerization, condensation or enzymatic reaction. Physical hydrogels can be prepared through methods such as freeze-thawing, ionic interaction by addition of counterions, hydrogen bonding, or heat-induced gelation.[155]

Hydrogels can also be classified based on properties such as the origin of the polymer, biodegradability, ionic charge or physical properties.[7,155–157] Based on the origin of the of the polymer, hydrogels can be further divided into natural (e.g., carrageenan, alginate, gelatin), synthetic (e.g., poly(acrylic acid), poly(vinyl alcohol)) and hybrid hydrogels (e.g., agar/polyacrylamide).[6,7,154,155,158] Each kind of gel has its own advantages: natural hydrogels tend to have excellent biocompatibility, synthetic hydrogels tend to be easier to scale or tune according to desired properties, and hybrid hydrogels exhibit advantages from both natural and synthetic ones.[6] Since hydrogels can be made up from a great number of different polymers their applications are very broad, going from agriculture, cosmetics and food industry to biosensors and tissue engineering.[7,154,159]

2.2.1. Carrageenan-based hydrogels

For the scope of this thesis (**Paper I, II & III**), we will focus on hydrogels based on the biopolymer κ-carrageenan, thus belonging to the group of natural hydrogels. Carrageenans are a family of polysaccharides that can be extracted from the *Rhodophyta* species of red seaweeds.[2] They belong to the hydrophilic linear sulfated galactans and different forms differ from each other in terms of number and placement of the sulphate ester groups.[2] Carrageenans mainly consist of alternating 3-linked β-D-galactopyranose and 4-linked α-D-galactopyranose or 4-linked 3,6-anhydro-α-D-galactopyranose, forming the repeating disaccharide unit of the structure.[2,160]

Traditionally, the carrageenans are split into six different types identified by a Greek prefix and the three most important ones from a commercial perspective are kappa (κ-), iota (ι-), and lambda (λ)-carrageenan.[2,5] Idealized structures of these three types of carrageenan can be seen in Figure 1.

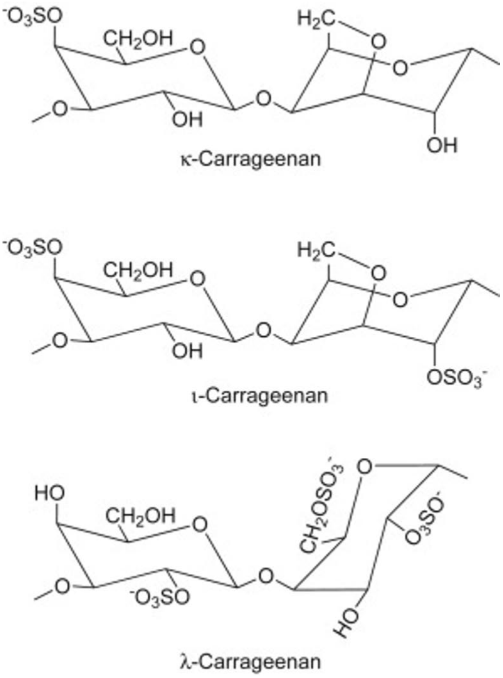

Figure 1. Idealized structure of the repeating unit of ι, κ and λ-carrageenan. Reprinted from Carbohydrate Chemistry for Food Scientists, 3rd edition, James N. BeMiller, Carrageenans, 279-291, Copyright 2019 AACCI, with permission from Elsevier.

The carrageenan molecules are anionic to their nature.[5] Many of their properties, such as solubility and gelation, are cation dependent and κ-carrageenan is often combined with potassium (K^+) for many of the applications in the food industry.[5,161] κ-carrageenan hydrogels are thermoreversible and physically crosslinked via junction zones or chain aggregates.[162–164] The gelation of κ-carrageenan hydrogels is cation dependent and the ability of cations to enhance the gelation follow the order of: $Li^+ < Na^+ \ll Mg^{2+}, Ca^{2+} < NH_4^+ < K^+, Cs^+ < Rb^+$.[160–162] For divalent cations, the ability to enhance gelation follow the order of: $Co^{2+} < Zn^{2+} < Mg^{2+} < Sr^{2+} < Ca^{2+} < Ba^{2+}$.[160] The gel strength depends greatly on the carrageenan concentration as well as the type and concentration of ions present.[162,163] The cations associated with κ-carrageenan within the work of this thesis are sodium (Na^+) and calcium (Ca^{2+}). However, the properties of pure salts of carrageenans might differ substantially from those of commercial carrageenans as even traces of other cations might alter the properties.[160]

The actual gel formation of κ-carrageenan is a complex process, affected for example by concentration, temperature and presence of ions.[160] A commonly accepted model of the gelation mechanism consists of two steps, the first one consisting of a temperature-induced coil-to-helix transition taking place upon cooling.[2,160,162,165] Subsequently, a cation-dependent aggregation takes place between the helices, forming physical crosslinks through ionic interaction and eventually a three-dimensional network is formed.[2,160,162,164,166] A schematic representation of the process can be found in Figure 2.

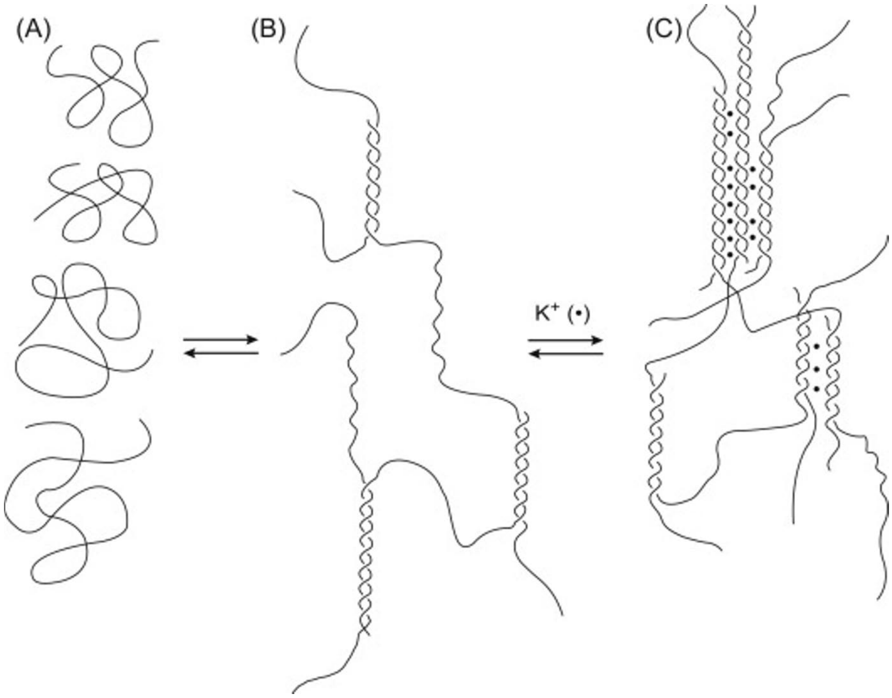

Figure 2. Schematic representation of the gelation process in carrageenan under the influence of potassium ions (K^+). Carrageenan molecules are in coiled state in hot solution (A), a coil-to-helix transition takes place upon cooling of the solution (B), the helices aggregate upon further cooling in the presence of cations (C). Reprinted from Carbohydrate Chemistry for Food Scientists, 3rd edition, James N. BeMiller, Carrageenans, 279-291, Copyright 2019 AACCI, with permission from Elsevier.

2.2.2. The use of hydrogels in teaching

Hydrogels have also found their way into teaching and have been used in regular laboratory teaching in schools, outreach activities as well as in at-home laboratory exercises.[167–169]. Sometimes the hydrogel is mainly used as a tool for improving a laboratory exercise or demonstration. Such is the case in the study by Stauffer and Fox, where hydrogels are used as a means to prevent rapid mixing of the colors produced at the electrodes during electrolysis of iron nails in the presence of indicators.[170] Other times the hydrogels are used to teach different aspects of chemistry, such as the connection between chemical bonding and the properties of a material, sustainability and resources or polymer science in general.[171–174] In some cases the actual structure of hydrogels has been used as a tool for teaching a concept, rather than the physical hydrogels themselves. Such is the case in the studies of Hanson et al. where the hydrogel structure is used to teach how the underlying structure will influence the mechanical properties on the macroscopic level.[175,176]

The use of hydrogels is an excellent way of incorporating everyday items into teaching. Hydrogels based on for example gelatin and alginate are non-toxic and easy to handle, also for students.[177,178] Additionally, they are cheap and easy to get a hold of for example in the form of diapers and contact lenses. They are versatile and can be used for teaching many of the main topics encountered in lower and upper secondary school chemistry and physics, such as pressure, light, equilibrium reactions and polymerization.[179] The appreciation of the hands-on and tactical experience that can be provided using hydrogels was high for example among the students that took part in the activities with the composite hydrogel developed by Warren et al.[180] Hydrogels can also be used for teaching more advanced topics such as drug delivery, sensing and tissue engineering.[167,171,181] This also makes them excellent tools for creating materials for courses intended to bridging the gap between upper secondary school and university, an important new aspect in the current Finnish curriculum for upper secondary school.[60,61]

Table 2 presents a compilation of some of the topics in high school (typically grade 8-12) chemistry that have been taught by utilizing hydrogels. In some cases, the hydrogel has been used as a tool, in others it has been the head number. Additionally, hydrogels have also been used for teaching topics within physics and biology as well as topics such as smart materials and bioplastics at university level [175,176,182–186]

Table 1. Examples of topics in chemistry that have been taught using hydrogels

Main topic	**Type of hydrogel**	**Reference**
Electrolysis	Gelatin	[170]
Polymer science	Alginate	[174]
Organic chemistry	Contact lenses	[169]
Drug delivery	Gelatin	[167]
Tissue engineering	Alginate	[171]
Chemical bonding, properties	Alginate	[172]
Chemical sensing	Poly(vinyl alcohol)	[181]
Recycling and resources	Alginate	[173]

2.3. Chemical gardens

The chemical gardens were first described by Johann Glauber in 1646 in his textbook *Furni Novi Philosophici*, in which he described them as growing in the form of plants and trees.[9,17,18] These so called classical chemical gardens consist of hollow structures formed by the precipitation that takes place after placing a seed of a metal salt into an aqueous solution of an anion such as silicate, carbonate, phosphate, oxalate or sulfide.[15,17,19] The silicate solution has been the most popular and most studied type and thus the chemical gardens are also known as silicate, silica, crystal or colloidal gardens[15,17] Although it should be mentioned that the term crystal garden might also describe experiments, for example in toy sets, intended for growing crystals. Chemical gardens have also been a popular classroom demonstration for a long time due to the beautiful structures formed especially when colorful metal salt are used, even though it can be argued that they are not very well suited for teaching due to the complex processes.[10,12–14,17,187] They still appear as suggested demonstrations or experiments, for example among the teaching resources (edu.rsc.org) provided by the Royal Society of Chemistry (RSC) and in the widely known *Chemical Demonstrations* by Shakhasiri.[10,188] A visual example of student-made chemical gardens can be seen in Figure 3.

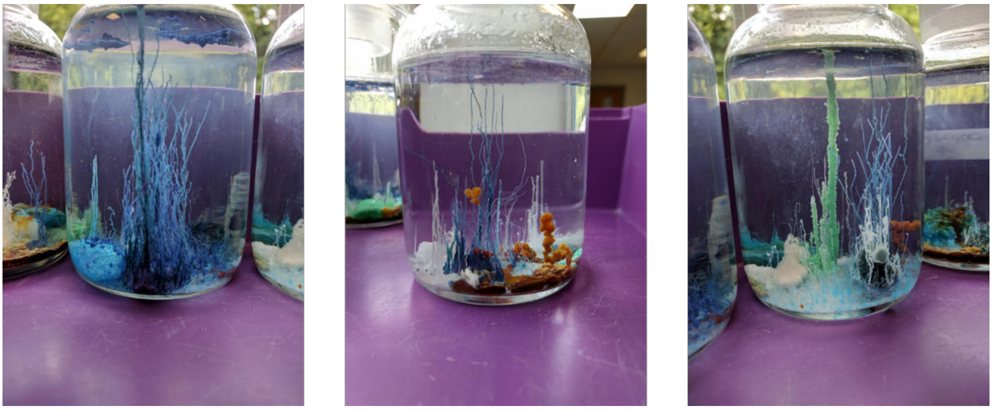

Figure 3. Visual examples of the classical metal-seed chemical garden made by students at Gordon's School[189]*, Surrey, England according to the instructions provided by the RSC.*[188] *Printed with permission from Gordon's School.*

Shakhasiri suggests *The Silicate Garden*-demonstration as an illustration of dynamic formation of solid phases, controlled by diffusion and osmosis, in a far-from-equilibrium system.[10] The RSC points out that the experiment with crystal gardens is one that continues to fascinate the students and suggest using the experiment for teaching introductory Earth science or the more practical aspects of laboratory work instead (setting up simple inquiries, reporting results, making and recording observations, using appropriate techniques).[188] The same reasoning is used by Matsuoka in an experiment where silica gel cat litter soaked in metal salt solutions is utilized as the seed.[190] Matsuoka argues that the experiment can be used not only for promoting curiosity but also to teach things such as basic experimental technique for middle school and differences in solubility for high school.[190] The chemical gardens can even be found as ready kits made for teaching purposes, such as the ones provided by Flinn Scientific[191] or Fischer scientific[192]. They are also popular in different kinds of chemistry sets and can be found among experiments in the MEL Science subscription kits[193] and sometimes marketed as magic rocks[194].

The formation of the classical chemical garden takes place due to osmotic and buoyancy forces.[9,15–17,195] A schematic of this growth process, known as seed growth, is presented in Figure 4.[9] The classical gardens use sodium silicate solutions as the external solution in to which the solid metal salt crystal (seed) is placed (Fig. 4a).[9,17,196] Other alkaline silicate solutions can also be used under the condition that the cation does not precipitate with the counterion of the metal in the salt being used.[17]

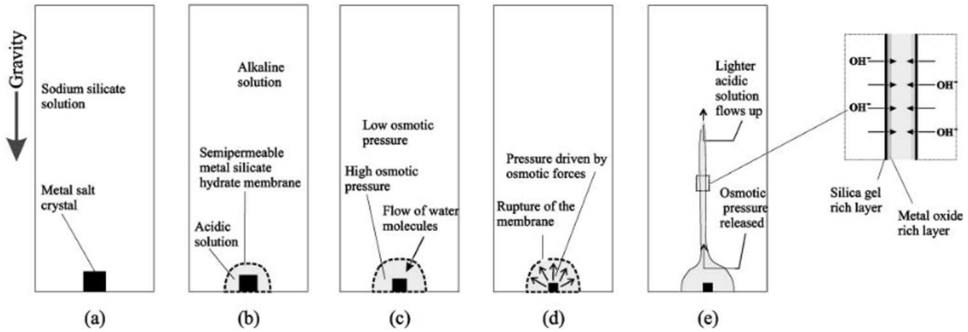

Figure 4. Schematic overview of the chemobrionic growth process. Reprinted from Journal of Colloid and Interface Science, 256, Cartwright et al., Formation of Chemical Gardens, 351-359, Copyright 2002, with permission from Elsevier.

As the metal salt crystal is placed in the silicate solution it starts dissolving and the released metal (M) ions will react with the silicate ions, forming a colloidal semipermeable membrane (Fig 4b, Equation 1).[15,17,19]

$$M^{2+}(aq) + \ Na_2SiO_3(aq) \rightarrow 2\ Na^{+}(aq) + MSiO_3(s) \qquad (1)$$

The developed membrane will restrict the exchange of molecules and ions between the internal solution containing the metal salt crystal and the external silicate solution.[9,15,17,196] The seed will continue dissolving, meaning that steep gradients of concentration are created, which leads to an increased osmotic pressure of the internal solution as water and hydroxide ions are drawn into it (Fig 4c).[9,15,17,196] The membrane will expand until eventually the pressure is release through the rupturing of the membrane (Fig 4d).[9,15,17] As this happens buoyancy forces will cause the jetted internal solution to flow upwards (Fig 4e) and when the silicate meets the internal solution of lower pH, precipitation takes place.[9,15,17] A tubular wall is formed, and the metal ions will precipitate in the inner part of wall, for example by forming metal hydroxides as described by Equation 2.[17]

$$M^{2+}(aq) + 2\ OH^{-}(aq) \rightarrow M(OH)_2(s) \qquad (2)$$

The semipermeable membrane is hereby re-established, an osmotic pressure is once again increasing over the membrane, and eventually it will rupture again.[17] The process and the growth of the tubes continues in cycles for as long as the system is in a non-equilibrium state.[9,15,17,195]

In addition to silicates, the external solution used for chemical gardens can also consist of anionic solutions such as carbonates, phosphates, chromates, borates, zincates, aluminates and cyanoferrates.[13,15] The anions should satisfy at least the conditions that they form a semipermeable membrane with the metal-salt seed and that they, at the pH of the internal solution form a precipitate with the cations present in said solution.[17] The classical chemical gardens with the seed growth is only one example of a chemobrionic system where chemical gardens can grow. Other examples of the experimental methods used within the chemobrionic research injection growth, bubble guidance, membrane growth, varying gravity and growth in gels.[17] The benefit of having such a variety of methods is that different techniques can be used to explore various aspects of the complex mechanism separately.[17]

The seed growth method has been used in the work presented in this thesis (**Paper II**, **Paper III**), where a gel loaded with ions was used to grow chemical garden structures. Apart from the solid seed of a metal salt, the seed can also consist of a pellet[197], polymer beads[198] or gels loaded with one of the reacting ions[199]. Examples can be found of growth from both planar[199–201] and non-planar[198,202] hydrogel surfaces, where the hydrogels have been loaded with cations layered or surrounded by anionic solutions. Using a gel as the seed offers the advantages obtaining micro sized tubes and of being able to measure quantitative parameters, such as the precipitate coverage, that can then be linked back to the theoretical expectations and thus give valuable information about the formation of the tubular structures.[200] Tubular structure with phases such as hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), calcite ($CaCO_3$), witherite ($BaCO_3$) and atacamite ($Cu_2Cl(OH)_3$) have been obtained utilizing a hydrogel seed.[199,200]

2.4. Calcium phosphates

The chemical gardens structures of interest to the thesis consist of CaPs. CaPs occur in a large variety, they are abundant in nature and living organisms as well as important materials in fields such as geology, biology, medicine, dentistry and in industry.[203,204] The applications of CaP materials range from biomedical materials, such as bone fillers, scaffolds in bone tissue engineering and drug delivery systems, to more industrial applications, such as catalysts, catalyst carriers, fertilizers and absorbents for the removal of pollutants.[203,205,206] Different CaPs exhibit variation in properties such as composition, structure, stability, solubility, molar Ca/P ratio and acidity/alkalinity.[203,204,207] They can be classified for example based on the type of phosphate anion present: ortho-(PO_4^{3-}), meta-(PO_3^-), pyro-($P_2O_7^{2-}$) or poly- ($(PO_3)_n^{n-}$) or by the number of hydrogen ions attached to a multicharged anion: mono-($Ca(H_2PO_4)_2$), di-($CaHPO_4$), tri-($Ca_3(PO_4)_2$ and tetra-($Ca_2P_2O_7$) CaPs. [203,204,207]

As the properties of a CaP compound affect their formation and functions, some are more suitable for certain applications than others.[204] The Ca/P molar ratio, for example, gives information of the acidity and water-solubility of the compound. The lower the molar ratio is, the more acidic and water-soluble the compound will be.[203] A few examples of CaPs, that will be seen also later in the thesis, are given in Table 3.[204,207]

Table 2. A list of some CaP compounds[204,207]

Compound	**Formula**	**Ca/P molar ratio**
Dicalcium phosphate dihydrate (DCPD) mineral brushite	$CaHPO_4 \cdot 2H_2O$	1.0
β-Tricalcium phosphate (β-TCP)	$\beta\text{-}Ca_3(PO_4)_2$	1.5
Amorphous calcium phosphates (ACP)	$Ca_XH_Y(PO_4)_Z \cdot NH_2O$ N=3-4.5; 15-20% H_2O	1.2–2.2
Calcium-deficient hydroxyapatite (CDHA)	$Ca_{10\text{-}X}(HPO_4)_X(PO_4)_{6\text{-}X}(OH)_{2\text{-}X}$ (0<X<1)	1.5–1.67
Hydroxyapatite (HA)	$Ca_{10}(PO_4)_6(OH)_2$	1.67
Carbonated apatite (CO_3A)	A- CO_3Ap: $Ca_{10}(PO_4)_6CO_3$ B- CO_3Ap: $Ca_{10}(PO_4)_{6\text{-}X}(CO_3)_{3X/2}(OH)_2$	

2.4.1. Calcium phosphates and hydrogels

For this thesis, the questions of interest were *if* and *what kinds* of CaPs could be grown from a κ-carrageenan hydrogel interface, rather than aiming for a certain type. The synthesis of CaP materials using hydrogels is not a new concept, even though the utilization of κ-carrageenan for growing chemical gardens consisting of CaP has, to the best of our knowledge, not been done earlier. For example, CaP composites and hybrid materials within hydrogels have been synthesized using gels based on polymers such as poly(ethylene oxide phosphonamidate)[208], alginate[209], poly(acrylic acid)[210], gelatin[211,212], ι-carrageenan[213] and κ-carrageenan[214]. The ι-carrageenan hydrogels were used to synthesized a micro-porous CaP composite.[213] The κ-carrageenan hydrogels were used to synthesized porous nanocomposite of κ-carrageenan and a mixture of CaPs (ACP, HA and CDHA).[214]

The CaPs that are of most interest within the scope of this thesis are those grown from gel/liquid interfaces. CaPs can be grown plainly at the hydrogel interface, for examples as spherical apatite particles obtained on the surface of a κ- and λ-carrageenan hydrogels.[215,216] However, of even more interest are tubular or chemical garden structures. Examples of tubular CaP structures grown from a gel/liquid interface can be found in works of Kamiya et al.[217] obtaining CDHA using an agar-based hydrogel, Tanahashi et al.[201] obtaining DCPD and HA using an agar-based hydrogel, and Ibsen et al.[199] obtaining apatite using a gelatin-based hydrogel. In all of these cases the hydrogels contained calcium ions and were layered with phosphate solutions.[199,201,217]

Extensive work on the subject has also been reported by Hughes et al., having presented several articles of chemical garden CaP structures grown from a hydrogel surface. Their work has provided insight into growth mechanism of the tubular structures, their potential use as cellular scaffolds and bone augmentation material, incorporation of pyrophosphate in the structure and controlled self-assembly.[20,200,202,218,219] CaP phases such as HA, DCPD and CDHA were obtained through the experiments.[20,200,202,218,219] In addition to planar hydrogel surfaces, their work has also involved creating hydrogel spheres from which tubular structures of HA and DCPD were obtained. These structures also showed promising results when assessed for their biocompatibility.[202] Their investigations showed that the concentration and the composition of the solution used, affects the rate of formation as well as number, length and microstructure of the tubes.[20,200,202,218] Variations in the concentration and composition give some control over the tubular formation, yet greater control is desired. In a more recent publication Hughes et al. managed to gain control over the height of the tubular growth by displacing the phosphate solution with water using a custom-built liquid exchange unit, which additionally proved to provide excellent opportunity for in situ purification of the tubular structures. Further, the custom-built unit also provided means of manufacturing a composite consisting of tubular structures within a 2-hydroxyethyl methacrylate (HEMA) hydrogel.[219] A compilation of the different CaPs that have been obtained from hydrogel surfaces can be found in Table 3.

Table 3. Examples of CaPs obtained by utilizing hydrogels

Type of hydrogel	**Obtained CaPs**[*]	**Ref.**
	CaPs on hydrogel surfaces	
κ-carrageenan	HA	[215]
κ-carrageenan	apatite	[216]
λ-carrageenan	apatite	[216]
	Tubular structures from gel/liquid interface	
Agar	CDHA	[217]
Agar	DCDP, HA	[201]
Gelatin	Apatite	[199]
Agar	CDHA	[20]
Agar	HA, DCPD	[200]
Agar	HA, DCPD	[202]
Agar	Amorphous apatitic calcium orthophosphate Calcium pyrophosphate	[218]
Agar	CDHA	[219]

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[*] As stated by the author

3. EXPERIMENTAL

3.1 Materials

For the teaching materials developed into the writing board experiments (**Paper I**) reagent grade κ-carrageenan, anhydrous magnesium sulfate and ammonium hydroxide were acquired from Sigma-Aldrich. Reagent grade hydrochloric acid was acquired from Merck, Germany. Food-grade κ-carrageenan (SpecialIngredients, UK) and Epsom salt (magnesium sulphate, Nortembio) were bought through Amazon. Red cabbage (*Brassica oleracea*), bilberry (European blueberries, *Vaccinium myrtillus*), vinegar, citric acid, baking soda and 9 V batteries were all purchased from a local supermarket.

For the chemical garden studies (**Paper II** and **III**) food-grade κ-carrageenan powder (SpecialIngredients, UK), was bought through Amazon. Analytical grade trisodium phosphate (tert) dodecahydrate ($Na_3PO_4{\cdot}12H_2O$), calcium chloride dihydrate ($CaCl_2{\cdot}2H_2O$), hydrochloric acid (HCl) 37% and sodium hydroxide (NaOH), were obtained from Merck, Germany. Ethanol (99.5 %) obtained from Altia, Finland.

All chemicals were used as received without any further purification.

3.2. Methods of preparation

3.2.1. Preparation of indicator juices

Indicator juices used in **Paper I** were prepared by chopping red cabbage or crushing bilberries before adding them to large beakers. Water was boiled using a water boiler and then immediately poured over the solid material. The mixtures were then left standing for an hour. The solid pieces were removed by pouring the mixture into a coffee press and thereafter, the filtrate into flasks. The red cabbage juice was made using 1200 ml of water and 450 grams of chopped, fresh red cabbage. The bilberry juice was made using 1200 ml of water and 300 grams of frozen bilberries.

3.2.2. Hydrogel preparations

The hydrogel for the writing board (**Paper I**) was prepared by adding 1.5 wt% of κ-carrageenan to a 0.09 M magnesium sulphate solution containing indicator juice. The 0.09 M solution was prepared as a mixture consisting of 60 vol% 0.15 M magnesium sulphate solution and 40 vol% indicator juice (prepared as described in Section 3.2.1.). The carrageenan was added slowly and carefully under stirring and heating (70 °C) so that no clots were formed. The pH of the solution was adjusted using vinegar, citric acid or baking soda according to the desired colour of the gel. When all the carrageenan had been added, the gel solution was removed from the heating plate and poured into suitable containers.

The basic preparation of the hydrogels for the chemobrionic studies (**Paper II** and **III**) was done as follows: a dispersion was created by stirring κ-carrageenan into a solution of 0.1 M calcium chloride (pH 4.5) or 0.1 M tri-sodium phosphate (pH 12.9) at room temperature. The dispersion was then heated and stirred simultaneously until a clearly solubilized solution, with a final temperature between 65–75 °C was obtained. The solubilized solutions were transferred into beakers and left standing at room temperature for cooling down and setting of the hydrogel.

This basic recipe was used as such for **Paper II** but modified slightly for **Paper III.** For **Paper III**, at the end of the heating 5 ml of DI water was added in the solubilized solution and the solution was stirred for an additional minute before being transferred into the beakers.

The amounts of κ-carrageenan used affected the heating and setting times needed when preparing the hydrogels. The parameters used for preparing the different types of hydrogels presented in this thesis were varied according to Table 5.

Table 4. Amounts of κ-carrageenan, heating and setting times used in the hydrogel preparations

Hydrogels for teaching purposes		
Paper I		
Amount of κ-carrageenan (wt%)	Heating time (min)	Setting time (min)
1.5	n.a.	n.a.
Phosphate-based hydrogels		
Paper II		
Amount of κ-carrageenan (wt%)	Heating time (min)	Setting time (min)
1.0	30	35
1.5	30	20
2.0	30	15
3.0	30	15
4.0	30	15
Paper III		
Amount of κ-carrageenan (wt%)	Heating time (min)	Setting time (min)
1.5	10	15
Calcium-based hydrogels		
Paper II		
Amount of κ-carrageenan (wt%)	Heating time (min)	Setting time (min)
1.5	30	30
Paper III		
Amount of κ-carrageenan (wt%)	Heating time (min)	Setting time (min)
1.5	30	15

3.2.3. Preparation of the hydrogel writing board

A Petri dish was prepared by placing a copper wire along the edges of the dish, leaving one end of the wire sticking up above the edge of the dish. The hot gel solution containing an indicator (see Section 3.2.2.) was then poured into the Petri dish and left to cool in room temperature for a few hours before moving them to a fridge for storing. A schematic picture of the set-up is given in Figure 5.

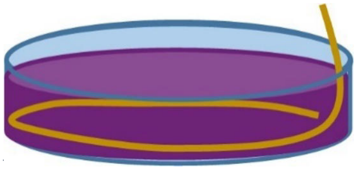


Figure 5. Schematic picture of the writing board-hydrogel. [Figure 1 (II) from ***Paper I****].*

3.2.4. Generating the chemical garden systems

After letting the hydrogels cool down and set according to the times given in Table 4, a counterion solution was layered on top of the hydrogel. For this thesis, two chemical garden systems were created:

- the P-gel system with a hydrogel containing phosphate ions
  and
- the Ca-gel system with a hydrogel containing calcium ions.

The P-gel system consisted of a hydrogel made from a 0.1 M tri-sodium phosphate solution (pH 12.9), layered with a counterion solution of 0.1 M calcium chloride (pH 4.5). The Ca-gel system consisted of a hydrogel made from a calcium chloride solution (pH 4.5), layered with a counterion solution of 0.05 M tri-sodium phosphate (pH 12.9). The hydrogels were layered with the counterion solution immediately when the setting time of the hydrogel had passed (see Table 4). A schematic illustration of the two systems is given in Figure 6.

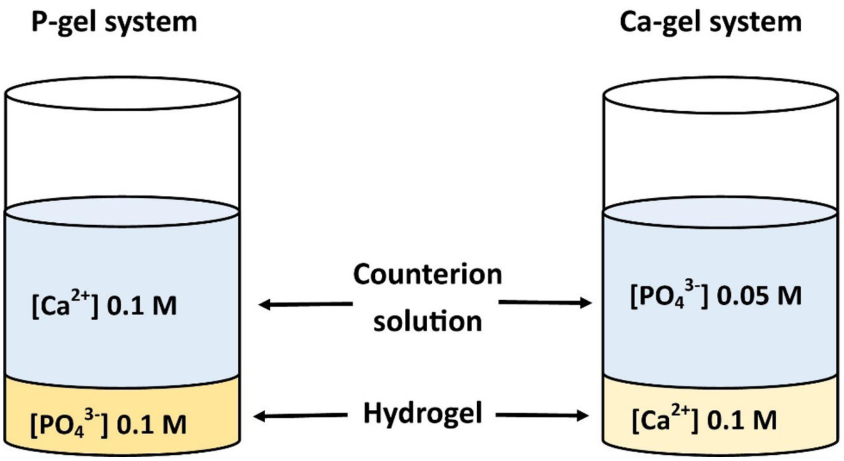


Figure 6. A schematic illustration of the two chemical garden systems used in this thesis. P-gel systems to the left and Ca-gel system to the right.

3.2.5. Sample preparations for characterization

Preparation of the tubular structures (tubes) grown in the chemical garden systems was done by transferring them from the beaker to a Petri dish using a plastic pipette. The tubes were rinsed twice with distilled water and then twice with ethanol (99.5%) to remove possible additional material (e.g., unreacted precursors and non-tubular products from reactions at the gel/liquid interface) or excess solution. The tubes were finally transferred to another Petri dish and left in room temperature overnight to dry.

3.3. Investigation of the chemical garden systems

The chemical garden systems were assessed by pH (starting values and changes), stiffness of the hydrogels (measured by amount of included κ-carrageenan) as well as relative height and shape of the grown tubular structures.

The pH was measured using a Metrohm 744 pH Meter (Metrohm Ltd., Switzerland). Measurements of the solutions were done using a solitrode electrode and of the hydrogels with a spearhead electrode with gel electrolyte. All measurements were done at room temperature. The pH changes of the systems were monitored for 60 min and recorded using GoPro Hero 7 Black camera (GoPro, Inc, USA). The pH probe was placed approximately 1 cm above the hydrogel surface during the entire measurement and afterwards the pH was logged and plotted for every two minutes. To avoid disturbances from the counter ion solution, the pH measurements of the hydrogels were performed at growth time of 0, 15, 30, 45 or 60 min after removing the counterion solution. Each growth time was measured on a separate gel, at four different places. The hydrogel surface was rinsed with water and gently dabbed dry with paper before pH measurement.

Since two working systems, related by inverting the ions in the hydrogel and counterion solution, were obtained, emphasis was put on comparing the two systems against each other. The chemical garden systems were also partly characterized by the properties of the tubular structures that were obtained.

3.4. Characterization of the chemobrionic structures

3.4.1. Methods and purpose of characterization

The tubes grown in **Paper II** and **III** were characterized using light microscopy, scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDS), X-ray diffraction (XRD) and thermogravimetric analysis (TGA). The tubes grown in **Paper III** were additionally characterized with atomic force microscopy (AFM). Before characterization, the tubes were washed as described in Section 3.2.5. Prior to measurements using X-ray diffraction and thermogravimetric analysis, each sample was ground into a fine powder in a mortar to ensure representative samples of the bulk composition. All characterization was done on intact tubes.

Light (or optical) microscopy can be used to examine the microstructure of a material.[220] The sample is illuminated and the light path is led through lenses, thereby creating a magnified image of the original sample.[220–222] A light microscope, using photons to illuminate and form an image of an object, can magnify objects approximately between 10 to 1500 times, details can be resolved down to about 0.2 µm.[222] For a stereomicroscope the magnification is regarded to be low to medium, usually between 5 to 45 times, and the sample is illuminated by reflected light.[221] In this thesis, an Olympus SZX12 stereomicroscope with a Nikon Coolpix camera was used to obtain magnified images of the tubes. The main purpose of these images was to display the macrostructures and sizes of the different kinds of tubes.

SEM uses an electron beam instead of light to scan the surface and obtain high-resolution information, such as topography and morphology, about the material.[220,223] The sample being analyzed should be conductive and therefore non-conductive samples are sputter coated with a thin layer of carbon or a metal such as gold.[223] For analyzing the elemental composition of a sample, EDS can be used to measure the X-ray spectrum produced by the electron beam interaction with the sample.[224] Silicon drift detector EDS (SDD-EDS) enables high level of accuracy in the detection of major and minor constituents even when there is peak interference in the obtained spectrum.[224] The SEM/EDS measurements for this thesis were performed with a LEO Gemini 1530 SEM (Zeiss Microscopy GmbH., Germany) with a Thermo Scientific Ultradry silicon drift detector EDS-system. The samples were placed on double-sided sticky carbon tape and sputtered with Pt (**Paper II**) or Au (**Paper III**). SEM was used to observe the cross-section and the outer surface of the tubes. By observing the cross-section of the tubes, information about the thickness of the walls, as well as the exterior and interior structures was obtained. EDS was used for elemental mapping with the primary aim of investigating the possible presence of κ-carrageenan in the tubes.

XRD is used for determining the crystal structure of materials. Diffraction methods do not use the elemental composition of a chemical compound for identification, but rather the crystalline structure.[220,225] This means that XRD can be used to identify different phases or different compounds with the same elemental composition. [220,225] The X-ray radiation used for measurements is monochromatic, usually from a Cu, Mo, Cr or Ag source.[220,225] The most commonly used radiation source in laboratory settings is Cu, particularly the K-α line.[220,225] The XRD measurements for this thesis were performed with a Bruker D8 Discovery X-ray diffractometer (Bruker-AXS, Germany) using CuKα-radiation (λ = 1,54 Å) in the 2θ range of 5/10 - 80° with a step size of 0.04°. The measurements for **Paper II** were done by placing the powders on a conventional sample holder belonging to the instrument. The measurements for **Paper III** were performed by placing the powders on double-sided sticky tape that had been attached to a microscope slide. Obtained diffractograms were matched against patterns from the ICDD database (2010 RDB PDF-2) using the EVA 2 software (Version: 16.0) by Bruker-AXS (Germany). The purpose of using XRD was to gain information about the crystal structures and phases present in the tubes, as well as gaining information about the possible maturation of the crystal phases with time spent in counterion solution.

In TGA, the mass of a sample is measured as a function of the temperature of the sample or as a function of time by using a sensitive thermobalance that is placed inside a furnace.[226] Typically, the sample is heated at a constant rate or kept at a constant temperature.[226] Different atmospheres can be used during the measurement (oxidizing, reactive or inert) and the choice affects which kind of events that can occur.[226] The measurement is also influenced by factors such as gas flow, heating rate, sample size and morphology, choice of crucible and changes in the sample's physical properties during the measurement.[226] Mass changes of the sample occur when it reacts with the surrounding atmosphere or loses material.[226] Mass loss or gain can for example occur due to evaporation of volatile constituents, desorption and adsorption of moisture, gases and volatile substances, loss of water of crystallization and thermal decomposition with the formation of gaseous products in an inert atmosphere. [226] The results gained from a TGA measurement are usually displayed by plotting mass or per cent mass against time and/or temperature in a so called TGA curve.[226] It is also common to plot the rate at which the mass changes.[226] In this case the first derivative of the TGA curve with respect to time or temperature is used and the plotted curve is called a DTG (differential thermogravimetric) curve.[226] The TGA analyzes reported in this thesis were conducted with a Netzsch STA 449 F1 Jupiter TGA (Netzsch, Germany). For **Paper II,** the main purpose of the TGA analysis was to investigate the presence of κ-carrageenan in the tubes and the temperature interval of 30 to 600 °C was used. For **Paper III**, the investigation was extended to include the possible presence of carbonate in the structure and the temperature interval was increased up to 1000 °C. The parameters for the TGA measurements for **Paper II** and **III** are summarized in Table 5.

Table 5. Specifications for the TGA measurement in ***Paper II*** *and* ***Paper III***

	Paper II	**Paper III**
Atmosphere	Nitrogen	Nitrogen
Gas flow rate	20 mL/min	20 mL/min
Temperature interval	30 – 600 °C	30 – 1000 °C
Heating rate	10 °C/min	5 °C/min
Crucible	Aluminum	Alumina

3.4.2. Other useful methods

The tubes were additionally characterized using AFM in **Paper III** to gain supplementary information about the exterior surface of the tubular structures and information about their stiffness. However, all measurements and analysis were performed by one of the co-authors, thereby excluding these measurements from the work done by the author of the thesis and the results presented here.

In addition to the methods already mentioned and used, both Raman spectroscopy and Fourier transformed infrared (FT-IR) spectroscopy could have given additional useful information. The use of Raman spectroscopy could help with identification and differentiation of different CaP phases based on the different peaks in the spectra caused by PO_4^{3-}, HPO_4^{2-} and $H_2PO_4^-$ groups, while the use of FT-IR spectroscopy could provide additional information about the presence of κ-carrageenan and carbonate within the tubular structures.[20,214,227] In addition to this, thermal treatment followed by characterization using XRD could also provide information of the CaP phases present in the tubes as CDHA will transform into β-TCP at temperatures above 800 ° C.[228] Table 6 summarizes the purpose of the methods that were used and gives short description of the information that could be provided by the other methods.

Table 6. Summary of characterizations methods used and presentation of other useful methods

<table>
<tr><th colspan="2">Characterization methods used</th></tr>
<tr><th>Method</th><th>Purpose</th></tr>
<tr><td>Light microscopy</td><td>Displaying macrostructure and size of the tubes.</td></tr>
<tr><td>SEM</td><td>Displaying cross-section and surface of the tubes in microscale.</td></tr>
<tr><td>EDS</td><td>Elemental mapping in search of the presence of κ-carrageenan.</td></tr>
<tr><td>XRD</td><td>Information about crystal structures and phases present in the tubes.</td></tr>
<tr><td>TGA</td><td>Information about possible presence of κ-carrageenan and calcium carbonate</td></tr>
<tr><td>(AFM)</td><td>(Information about exterior surface and stiffness)</td></tr>
<tr><th colspan="2">Other useful methods</th></tr>
<tr><th>Method</th><th>Information provided</th></tr>
<tr><td>Raman</td><td>Identification and differentiation of CaP phases[20]</td></tr>
<tr><td>FT-IR</td><td>Presence of κ-carrageenan and carbonate[214,227]</td></tr>
</table>

4. SHORT SUMMARIES OF THE ARTICLES

4.1. Paper I

In this work, red cabbage juice and κ-carrageenan were used to develop an environmentally friendly writing board intended for outreach activities and for teaching electrochemistry. The development was purposely done using uncomplicated procedures and by using only easily accessible materials and chemicals. The writing board concept as an outreach activity was evaluated by two groups of upper secondary school student visiting the Faculty of Science and Engineering at ÅAU. The evaluation showed that the students enjoyed the writing board and the creative touch involved in the work. Afterward an activity sheet aimed for classroom use was also developed but could not be evaluated due to the COVID-19 pandemic.

4.2. Paper II

In this work, the basis of two chemical garden systems producing tubular CaP structures from the interface of a κ-carrageenan-based hydrogel were established: one system with a phosphate-based hydrogel and a calcium-based counterion solution and a second system with a calcium-hydrogel and a phosphate-based counterion solution. The tubes obtained from the two systems were compared to each other based on characterizations done using light microscopy, SEM/EDS, XRD and TGA. The effect of hydrogel stiffness (amount of κ-carrageenan) on the macroscopic structures were evaluated using phosphate-based hydrogels. The tubes from the stiffness study were characterized using light microscopy (macroscopic size) and SEM (the walls of the structures).

4.3. Paper III

In this work, the two chemical garden systems from **Paper II** were further analyzed by measuring changes in pH of the hydrogel and counterion solution during the growth. Further, tubes in both systems were kept in counterion solutions for 1, 7, 14 or 28 days and were thereafter characterized using light microscopy, SEM/EDS, XRD, TGA and AFM. The temperature interval for the TGA measurement was extended to provide additional information. The tubes were investigated in terms of evaluating the structures from each system as well as for evaluating changes of properties as a function of time spent in the counterions solution.

5. RESULTS AND DISCUSSION

5.1. Hydrogels for teaching purposes

The aim of **Paper I** was to develop a teaching tool using uncomplicated procedures as well as cheap, easily accessible materials and chemicals. The hydrogels developed in **Paper II** and **Paper III** were also developed using uncomplicated procedures and equipment as well as easily accessible chemicals to make it possible to include them in teaching and outreach.

5.1.1. Set-up of the writing board experiment

The writing board concept uses a colorimetric hydrogel based on natural pH indicators for writing. The writing is done by utilizing the hydrogel as both an electrolyte as well as a pH indicator during the electrolysis of water. The materials needed both for the teacher (preparation of the writing board) and for the student (during the experiment) are found in Table 7.

Table 7. Materials used in the writing board experiment

For the teacher	For the students
• Indicator juice • K-carrageenan • Magnesium sulphate (Epsom salt) • Copper wire • Beaker • Stirring hot plate • Magnetic stirrer • Dish for the gel (assembly of the board)	• Petri dish containing red cabbage gel and copper wire • Nine-volt battery • Two wires with alligator clips • Copper wire-pen

The hydrogel is contained in a Petri dish with a copper wire inside the hydrogel. The writing on the board is done by attaching this copper wire to one terminal of a nine-volt battery, while attaching a piece of straight copper wire to the other. The attachment of the wires was accomplished using alligator clip wires. The straight copper wire (outside the hydrogel) is then used as the pen. A small bend at the unattached end made it possible to write by applying it gently to the hydrogel surface without destroying the hydrogel. The firmer the hydrogel, the easier it is to use for writing. Only a light touch should be used, but it might take some practice for some of the students. A schematic representation of the preparation and writing process is seen in Figure 7.

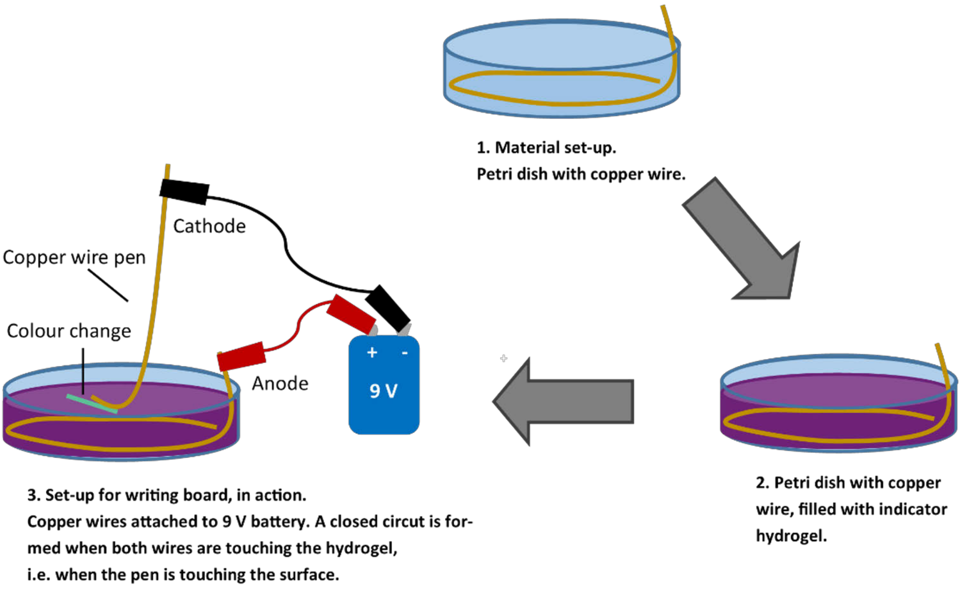


Figure 7. Schematic representation of the preparation and working principle of the hydrogel writing board. [Figure adapted from Figure 1, ***Paper I****]*

The hydrogel was prepared using magnesium sulfate, which acts as an inert electrolyte, and so the electrolysis of water in our hydrogel is described by the half-reactions given by Equation (2) and (3):

Anode $2\,H_2O\,(l) \rightarrow O_2(g) + \mathbf{4\,H^+}\,(aq) + 4\,e^-$ (2)

Cathode $4\,H_2O\,(l) + 4\,e^- \rightarrow 2\,H_2\,(g) + \mathbf{4\,OH^-}\,(aq)$ (3)

The writing is accomplished due to the color changes of the indicator in the hydrogel as the pH changes at the electrodes (indicated in bold in Eq 2 and 3).

A more user-friendly and nicer looking pen was made for visiting students by removing everything but the shell from a ballpoint pen, sticking the straight wire through it and stabilizing it with adhesive putty (Figure 8A). All the material that was provided for the students while evaluating the experiment is presented in Figure 8B.

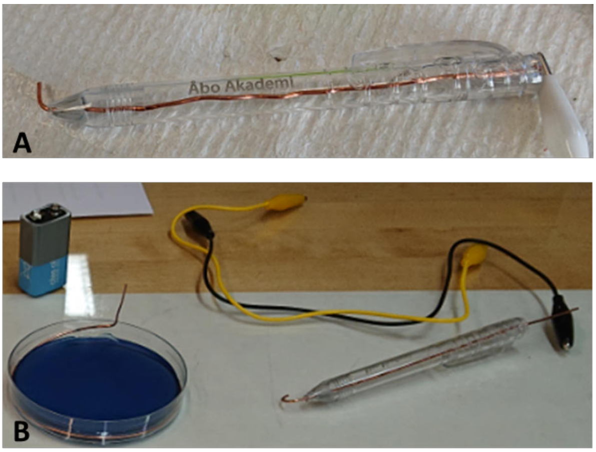


*Figure 8. The design of our custom-made copper pen used by the students for writing. An alligator clip is attached in the rear end of the pen (A). The material provided to the students during the lab session; 9 V battery, copper pen, alligator clips and pH indicator hydrogel containing a copper wire (B). [Figure 2, **Paper I**].*

Use of natural indicators, Epsom salt and commercial κ-carrageenan was motivated by showcasing the chemistry all around us and to make the experiment accessible to teachers. The use of food items made the experiment non-toxic, biodegradable, environmentally friendly and cost effective regarding both purchase and waste handling. The average cost for a 1 cm thick hydrogel made with commercial chemicals in a 90 mm petri dish, including the copper wire, was 0.28 euros in 2019. The petri dish and the battery were not included in the price. The choice of materials also makes the experiment accessible for teachers without a laboratory (e.g., in elementary school) as well as for students who want to continue the experiment at home. Epsom salt (Magnesium sulfate) was also inexpensive, non-toxic, biodegradable, easily obtainable and easy to handle. Sodium sulphate is more commonly used for the electrolysis of water especially when pH determination is also important.[229] In the present case, the Epsom salt was not only cheap and easy to obtain but additionally the magnesium ion (Mg^{2+}) also enhances the gelation of the κ-carrageenan more than the sodium ion (Na^{+}).[160]

5.1.2. Writing board experiment with students

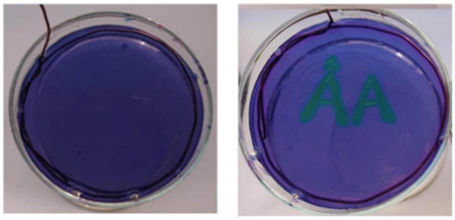
Two similar work sheets with work instructions for the writing board activity were developed, one for outreach activity (Appendix 1) and one for classroom teaching (Appendix 2). The outreach activity took the limited amount of time usually available during the school visits into consideration. The work sheet for classroom setting aimed at guiding and supporting students struggling with the concepts of the work better and was developed based on experienced gained from the school visits and discussions with the visiting students. Unfortunately, due to the COVID-19 pandemic we were only able to evaluate a trial version of the outreach sheet with upper secondary school students. It was neither possible to try the writing board experiment in classroom setting, with younger students or to try any revised version of the outreach activity.

During the outreach activity, the concept of the writing board has been introduced to the students as a challenge with the following three tasks:

- Can you write your name in the hydrogel in such a way that scratching the gel is not your main form of producing the letters?
- How many different colors can you produce in the hydrogel?
- Can you tell which terminal of the battery you have used for writing?

Some clues were given for the task: Equation (2) and (3) presented earlier, a colored pH scale for red cabbage juice and a list of the available materials. Only the Petri dish with hydrogel and copper wire were assembled beforehand. The terminals of the batteries provided were hidden beneath duct tape for the sake of the third task. Examples of writing on the pH responsive hydrogel, done by the author, is shown in Figure 9.

Red cabbage



Before After

Bilberry

Before After

*Figure 9. Red cabbage and bilberry hydrogels before and after writing "ÅA" using electrolysis. [Figure 3, **Paper I**].*

5.1.3. Student evaluation of the writing board experiment

The writing board experiment was evaluated in practice by 33 students in two different groups (from three different schools) where the students filled out a questionnaire in the end of the session. One of the groups was a Swedish-language Finnish school (questionnaire in Swedish) and the other group consisted of students from a Finnish-language Finnish school and a German school (questionnaire in English). The questions used in the English questionnaire are presented in Table 9.

Table 8. Presentation of the questions included in the evaluation questionnaire

Questions used in the evaluation questionnaire
Have you encountered any of these before: Electrolysis of water (demonstration) (Y/N) Electrolysis of water (lab work) (Y/N) Electrolysis of water using an indicator (demonstration) (Y/N) Electrolysis of water using an indicator (lab work) (Y/N)
Did you like the concept of the writing board?
Was it an interesting way of presenting Chemistry?
Did you understand what was happening/what you were doing?
Did you learn anything from it?
Any other comments regarding the writing board?

The distribution of the total number of answers to most of the questions are given in Figure 10 and Figure 11. All the participating students responded to the questionnaire in some way. However, not everyone answered every question and a few students answered in pairs. As this was intended to only be a trial before a more thorough evaluation, we did not interfere with those wanting to fill out the questionnaire together. Answers including the word “yes” were grouped together in one category, answers that did not include the word yes but were still positive and included word such as “okay”, “kind of”, “so so” were grouped into one category. Negative responses including the word “no” would have been a third category and otherwise negative without including the word “no” a fourth. However, no responses fitting with the negative categories were received. Additionally, among the freely given comments about the work, answers such as the following were found: “*it was fun*”, “*it was a very interesting technique*”, “*it was a good way of making it interesting*”, “*I don’t like chemistry at all but this was a good way to make it interesting”.*

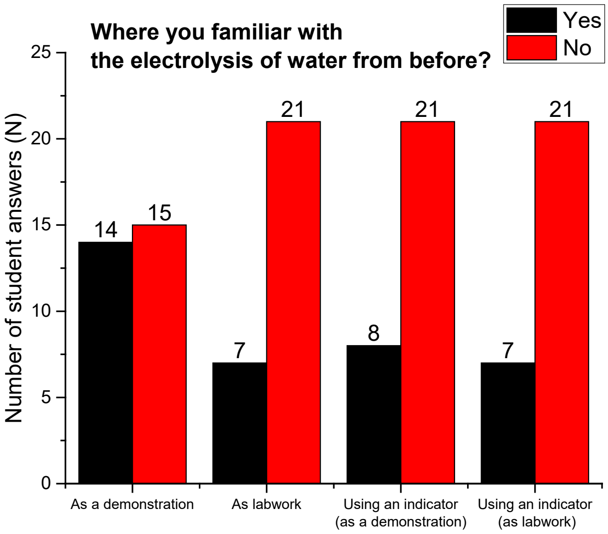


Figure 10. Results from the questions regarding earlier experience of the electrolysis of water. [Redrawn version of Figure 5A, ***Paper I****].*

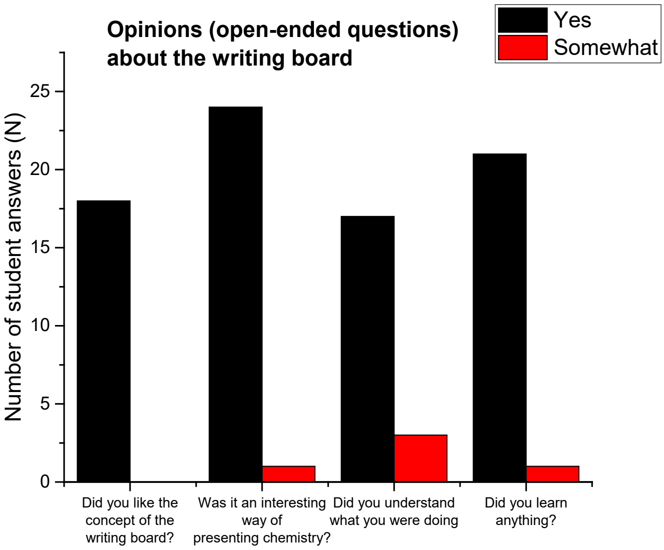


Figure 11. Results from the open-ended questions about the experiences of working with the writing board. [Redrawn version of Figure 5B, ***Paper I****].*

The results showed that about 50 % of the students were familiar with the electrolysis of water in the form of a demonstration, but only 25 % had performed any lab work of the topic on their own. The answers to the open questions were very positive and our assessment on site was that the students really enjoyed the artistic elements of the experiment as well as the freedom of creativity of the experiment. Even though only a small-scale trial could be conducted, we could at least see that the experiment seemed to trigger a situational interest in the topic. The positive outcome of combining science and art, as well as the benefits of using everyday items has been addressed by several authors.[230–232] As at least some of the students were familiar with the electrolysis of water from the chemistry lessons there definitely seems to be potential to introduce the concept of the writing board to Finnish chemistry classrooms.

5.1.4. Additional experiments with the pH responsive hydrogel

The indicator hydrogel was further used as a substrate for making stencil pictures by exposing it to gases (Figure 12). The stencils used for the pictures presented here were made by cutting out the wanted figures from parafilm. Using the stencils, the hydrogel was exposed to acid or basic gases according to the wanted color. For the shown examples hydrochloric acid (red) and ammonia (green/yellow) were used. The stencils can be made by students but the gas exposure, which must be done in a fume hood, should be left to the teacher and only after taking proper safety precaution. The hydrogels should then be left in the fume hood for a while after the exposure.

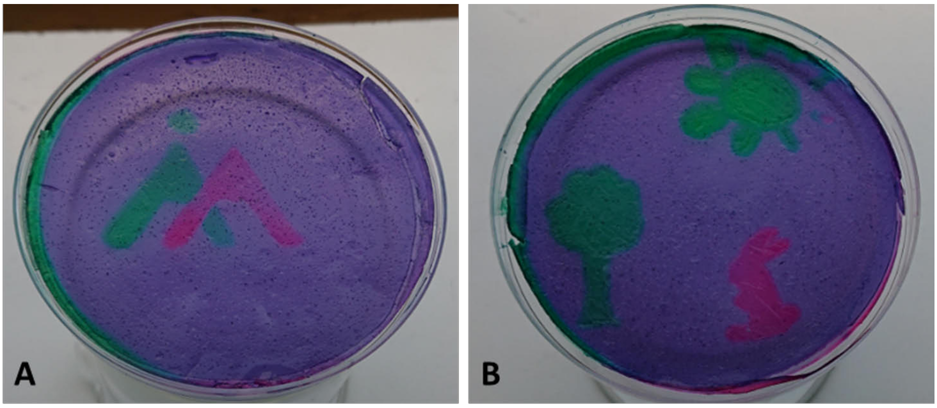


*Figure 12. Pictures of the letters "ÅA" (A) and random art (B) made using stencils and exposure to gaseous hydrochloric acid (resulting in red color) and ammonia (resulting in green color). [Figure 4, **Paper I**].*

The pH reactivity of red cabbage is a popular approach to combine chemistry with the making of art in the form of patterns and paintings.[233–236] The hydrogel allows for the gases to penetrate and dissolve into it, causing the color change. It is possible that the hydrogel can be used also for painting with aqueous solution of different pH, but we have not tried this setup. As the hydrogel had the benefit and opportunity of introducing another type of technique, we focused barely on the stencils.

Gelatin-based hydrogels have been utilized for illustrating different types of color changes. One example, also associated with electrolysis of water at iron nails, used 1,10-phenanthroline and thymolphthalein for the detection of Fe^{2+} and OH^-.[170] Electrolysis of water has also been demonstrated with microfluidic devices made from gelatin hydrogels.[229] Since our hydrogel is transparent in its native form (i.e., without any indicators present) there is also potential for it to be utilized also for these kinds of experiments as well as for other color changing reactions.

5.1.5. Further development of the hydrogel teaching concepts

The experimental procedure of the hydrogel writing board is easily scalable for different kinds of student groups and the experiment (including hydrogel preparation) can be done practically anywhere by teachers as well as students. It is also an excellent concept for different kinds of outreach activities as it is safe, does not require advanced/expensive equipment and does not produce hazardous waste. The writing board thus as great potential to be used even further in different kinds of settings if the work sheet is adapted.

Student groups visiting the Faculty of Science and Engineering at ÅAU usually have very limited time available. This makes it difficult to engage in any further discussions in connection to the writing board activity. However, with more time available or in a classroom setting, there are excellent opportunities to take the work further by discussing topics such as green chemistry and the need for reducing waste, especially hazardous such. The Petri dish used in the experiment, whether plastic or glass, can and should be cleaned and reused in other experiments. Plastic as a material has gained a lot of negative publicity in recent times and can be exchanged for something more recyclable like a drink carton. The battery can be exchanged for a small hand driven motor or solar cell.

Even though the chemical gardens systems were developed with outreach and teaching in mind, the pandemic hindered any evaluation of the concept. There is still great potential in the concept. The reaction times of the created systems is fairly short and the experiments could for example be used to teach the more practical aspects of laboratory work as suggested by the RSC.[188] With longer visits, characterization methods, such as spectroscopy and SEM, could also be included.

Both the hydrogel writing board and the chemical garden concept also have great potential to be developed into larger and longer activities. In a Finnish study university students majoring in chemistry gave interest in environmental issues as one of the reasons for their choice of major subject.[146] Both the concepts developed in this thesis could be used as a starting point for discussing green chemistry and sustainability. Students in the upper secondary age tend to show interest in topics related to health, sustainability, contemporary issues and future challenges.[57,237] This is well in line with the Strategic Research Profiles at the Faculty of Science and Engineering at ÅAU. The activities presented here could be combined with further activities together with other aspects of hydrogel research done at the Laboratory of Molecular Science and Engineering, the Laboratory of Natural Materials Technology and Pharmacy.[238–241] Thereby enhancing the number of topics in one activity, while also presenting more of the faculty's study programs and research. The chemical garden concept, as such or in a larger activity, is also a way to include actual research in the outreach which has been proven to increase both interest and learning.[107,108] The chemical garden concepts of this thesis intended for the students to do themselves could very well be combined with systems developed by others, for example Hughes et al.[200]

Additionally, a truthful picture of what the studies actually entail helps retaining the students that decide to start a study program.[120] Activities extended over longer periods of time could further help with increasing interest in a future STEM career as well as enhance learning.[107,108] Many of the suggestions provided in this section are in line with how Swedish upper secondary school students wished to improve their chemistry education.[78,151] Additional gain from the activities could be reached by engaging students from different stages of education to act as role models. [107,123,124]

5.2. Chemical garden studies

Paper II served as a first investigation into the possibility of growing tubular CaP structures from κ-carrageenan-based hydrogels. This was successfully accomplished and a first investigation of the properties of the CaP tubes grown from two kinds of κ-carrageenan-based chemical garden systems was done. In the work of **Paper III** further investigations were done of the obtained tubes as well as possible changes of these properties with increased time spent in the counterion solution. For **Paper III** some changes were made in the measurement parameters. These are found in Table 10 and Table 9.

*Table 9. Overview of changes in measurement parameters between **Paper II** and **III***

Characterization method	**Changes in parameters**
TGA	Temperature interval, heating rate, crucible
XRD	Sample holder

5.3. Properties of the chemobrionic systems

Others have shown that the concentration of the counterion solution affects the tubular growth.[20,200,202] However, in this study the concentration in itself was not a parameter of interest. The initial aim was to keep the two systems as alike as possible and therefore both the combination of a 0.1 M phosphate gel with a 0.05 M calcium solution and 0.1 M calcium gel with a 0.1 M phosphate solution were tested. Neither one of these were successful.

5.3.1. pH in the two systems

The pH of both hydrogels and counterion solutions in the chemobrionic systems were investigated as the pH difference between them is one of the factors affecting the growth process.[17,219] The obtained results of the measurements during the first 60 min after layering the hydrogel with the solution are provided in Figure 13.

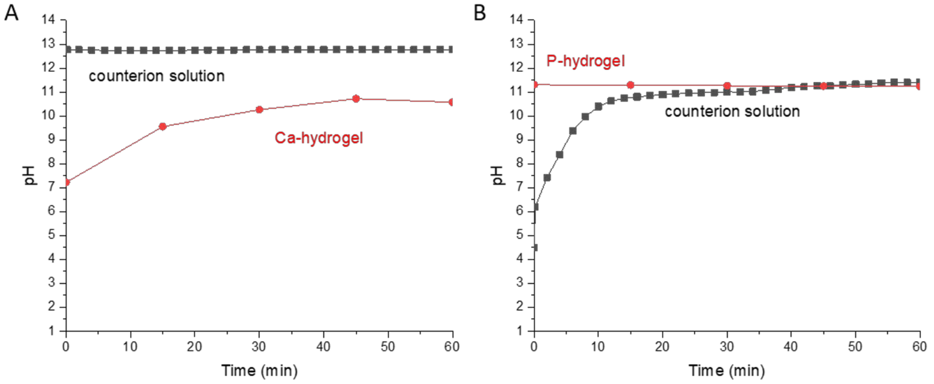


Figure 13. Changes in pH of both the counterion solution and the hydrogel during the first 60 min of growth in the Ca-gel system (A) and P-gel system (B). [Figure 2, ***Paper III****].*

Clear differences in the behavior of the two systems could be observed. After an initial increase in pH from about 7 to 10.7 in the Ca-gel hydrogel, the difference in pH between the hydrogel and its counterion solution (pH 12.8) was maintained during the entire observed period (ΔpH ~2.1). Meanwhile, for the P-gel system, the pH of the counterion solution changed very rapidly and reached the same pH value as the hydrogel within 45 min. As there is no pH difference between the hydrogel (pH 11.3) and the counterion solution (pH 11.3 at 44 min) anymore, there is also no driving force of the growth process.[199,218] This can at least partly explain the limited growth period of the P-gel system.

The graph in Figure 13B illustrates the rapid change in pH of the P-gel counterion solution as soon as it encounters the hydrogel. κ-carrageenan hydrogels are known to exhibit syneresis, which is a process where fluid is spontaneously released from the gel.[242] Presumably, this would likely push both OH^- and PO_4^{3-} ions out of the hydrogel, since these ions are not fixed in the hydrogel matrix by the polysaccharide. This is contrary to the Ca^{2+} ions, which are fixed in the Ca-hydrogel matrix as they are participating in the buildup of the hydrogel itself.

Thus, the mobile PO_4^{3-} ions in the P-gel system would form a thicker and coarser membrane on top of the hydrogel in contact with the counterion solution, compared to the more strongly bonded Ca^{2+} ions in the Ca-gel system.

5.3.2. The growth process of the tubes

The focus of the investigations was on the two systems created with 1.5 wt% κ-carrageenan hydrogels. These were created in both **Paper II** and **III.** Images of the tubes from **Paper III** are presented in Figure 14.

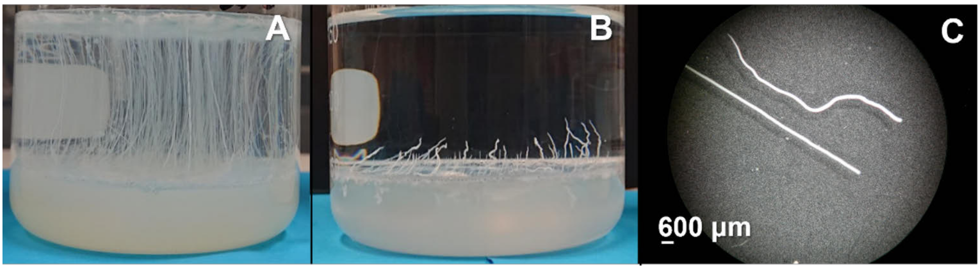


*Figure 14. The growth in 1 day of Ca-gel (A) and P-gel (B) showcased in 250 ml beakers with a diameter of 7 cm; a microscopy images (C) of a P-gel tube (top) and a Ca-gel tube (bottom) after 1-day growth. [Figure 1, **Paper III**].*

When comparing the tubes in the Ca-gel systems (Figure 14A) and P-gel system (Figure 14B), the Ca-gel tubes are longer, straighter and thinner than the P-gel tubes. This if further confirmed by the microscopy images in Figure 14C. While both tube types grew upwards, the P-gel tubes had clear kinks giving them a more crooked structure and the tube from a Ca-gel system is completely straight. This difference in macrostructure can be attributed to the speed of the growth process.[201] As the Ca-gel tubes grew substantially faster than the P-gel tubes, more solution would be jetted each time and the semipermeable membrane formed on the tube after each ejection of fluid would not grow as thick. In this case, the large osmotic pressure would break the tubes in the top when more calcium solution from the hydrogel was ejected into the phosphate solution. The P-gel tubes, however, grew more slowly and thus the semipermeable membrane grew thicker and was subsequently more likely to break at random places, as the phosphate solution from the hydrogel would be ejected.

The reason for this could hypothetically be explained by a thicker (and perhaps impermeable) membrane forming on top of the P-gel, which can hinder the movement of solvent (water molecules) from liquid phase to the gel phase to build up pressure. We therefore assume a low osmotic pressure within the P-gel, leading to shorter tubes. Further, even though the κ-carrageenan forms a complex with the Ca^{2+} ions, we do not expect all the Ca^{2+} ions present in the aqueous solution used for making the gel to be bound in the matrix. Additionally, as some of the ions are bound, we would expect the solution being jetted from the gel/liquid interface to have a lower density, thereby shooting further up into the layering solution. Thus, still leading to longer tubes in the Ca-gel system.

The observed growth in length for the P-gel tubes stopped within a few hours, while the Ca-gel tubes continued to grow for an extended period. The P-gel tubes thus remained fully immersed in the liquid, while the Ca-gel tubes reached all the way to the surface of the counterion solution. Thus, resulting in structures stemming from the tubes assembling along the surface (Figure 15).

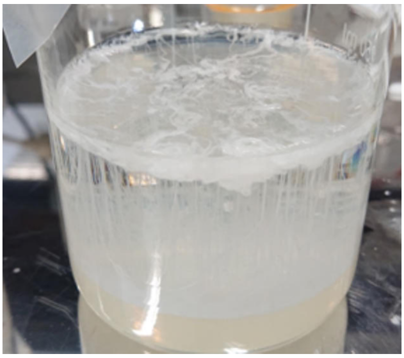


*Figure 15. Example of how the Ca-gel tubes continue to grow along the surface of the counterion solution in a structural layer. [Figure S1A, **Paper II**].*

In **Paper II,** the tubes were removed before they could reach the surface, in order to avoid possible contamination of this surface layer within our samples. The tubes from the Ca-gel were removed after 3 h while the tubes from the P-gel where remove after 1 day. In **Paper III,** the surface layer was removed and analyzed separately. The analysis confirmed that no contamination was present after the washing. For **Paper III,** the Ca-gel and P-gel tubes could thereby be removed after the same amount of time.

For **Paper II,** P-gel systems with 1 wt%, 2 wt%, 3 wt% and 4 wt% κ-carrageenan hydrogels were also created. The P-gel system was chosen as these tubes all remained fully in the liquid. The tubes grew thinner with increased amount of κ-carrageenan in the hydrogel. Camera and microscopy images of these tubes are presented in Figure 16.

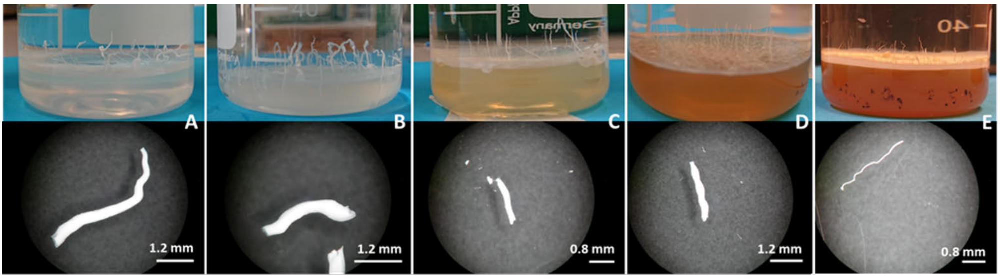


*Figure 16. Images of the tubes grown in P-gel systems with 1 wt% (A), 1.5 wt% (B), 2 wt% (C), 3 wt% (D) and 4 wt% (E) κ-carrageenan. Images were obtained with camera (top row) and optical microscope (bottom row). [Figure S2, **Paper II**].*

5.4. Properties of the tubes

All results presented henceforth are from 1.5 wt% κ-carrageenan systems if not otherwise stated. Samples will be referred to according to the time spent in counterion solution and the paper in which they appear in accordance with Table 10.

Table 10. Naming system for the samples presented in section 5.4

	Paper II	**Paper III**
Ca-gel tubes	3h (II)	1 day (III)
		7 days (III)
		14 days (III)
		28 days (III)
P-gel tubes	1 day (II)	1 day (III)
		7 days (III)
		14 days (III)
		28 days (III)

5.4.1. Morphology

We have already established that the Ca-gel tubes were longer, thinner and straighter than the P-gel tubes (section 5.3.3). The difference in tubes thickness is further confirmed by the tube diameters from **Paper II** seen in the SEM micrographs of Figure 17.

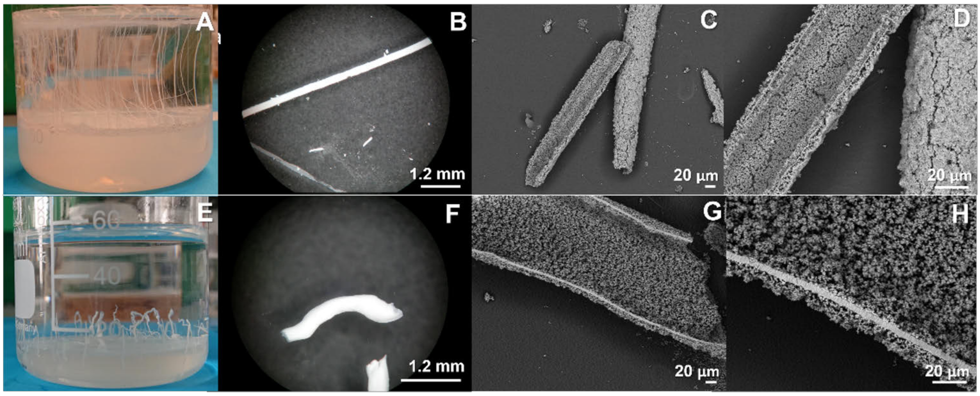


Figure 17. Collection of images acquired with different methods of the tubes grown in the Ca-gel (II) system (A-D) and P-gel (II) system (E-H). Images obtained with camera (A & E), optical microscope (B & F) and SEM (C, D, G & H). [Figure 1, ***Paper II****].*

Differences were also seen in the porosity, thickness of the walls and the precipitate structure of the interior and exterior surfaces (Figure 18). The P-gel tube further appears more porous, but the mid-layer of the P-gel tube (~2 µm) is much thicker compared to that of the Ca-gel (<0.5 µm).

SEM micrographs with greater magnification of the P-gel (II) tubes from the 1.5 wt% κ-carrageenan systems (Figure 18) exhibit clear differences in the exterior and interior structures. Three main regions could be identified: the exterior of the tube, the wall of the tube and the interior of the tube.

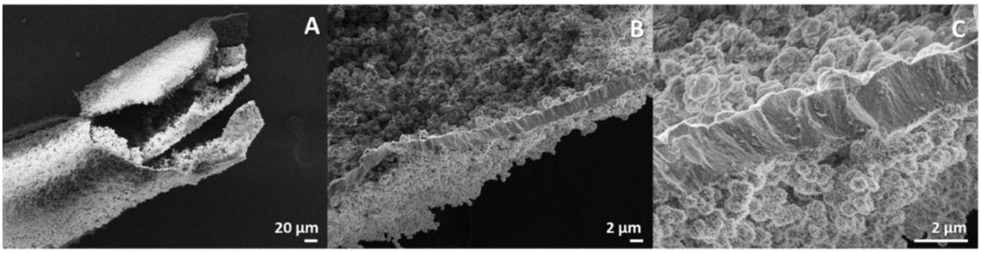


Figure 18. SEM micrographs at different magnification of 1 day (II) P-gel tube. Images of the tube at 250x (A), the tube wall at 2.5kx (B) and a close-up of the tube wall at 10kx (C) showing differences in the structure of the interior and exterior wall. [Figure S4, ***Paper II****].*

The differences of the three main regions of the tubes found in **Paper II** gave reason to investigate this further in **Paper III**. SEM micrographs (Figure 19) of cross-sections of the P-gel (III) tubes revealed the same three main regions with difference in the structure of each region. Visual examples of tubes after 1 day in counterion solution (left column) and 28 days in counterion solution (right column) are given in Figure 19 and visual examples of all four investigated time points are given in Figure 20.

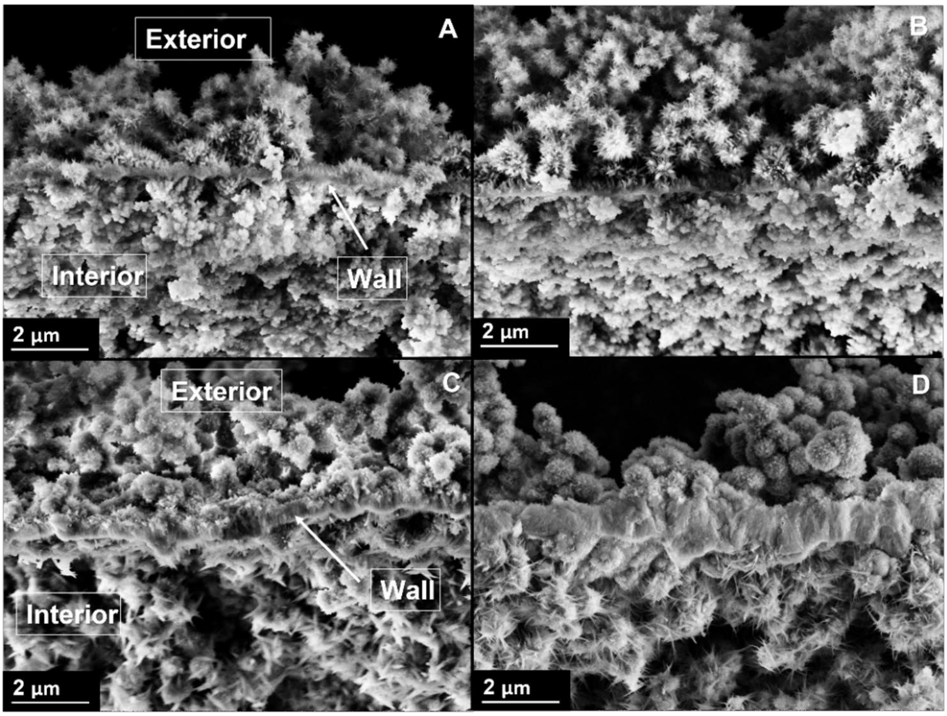


Figure 19. SEM micrographs at 10kx magnification of tubes that have been kept in counterion solution for 1 day or 28 days: Ca-gel 1 day (III) (A), Ca-gel 28 days (III) (B), P-gel 1 day (III) (C) and P-gel 28 days (III) (D). [Figure 3, ***Paper III****].*

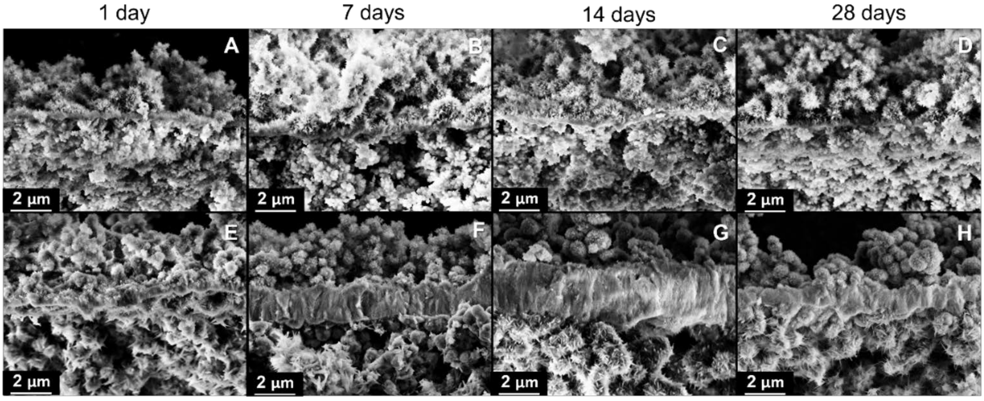


Figure 20. SEM micrographs at 10kx magnification of Ca-gel (III) tubes (upper row) and P-gel (III) tubes (lower row). The different tubes have been in counterion solution for 1 day (A&E), 7 days (B&F), 14 days (C&G) and 28 days (D&H). [Figure S3, ***Paper III****]*

When comparing the SEM micrographs of the two types of tubes, some differences in morphology could be observed; for instance, the Ca-gel (III) tubes had much thinner walls than the P-gel (III) tubes. The thickness of the P-gel tube walls varies from approx. 0.5–3 µm (Figure 20E–20H). Furthermore, the P-gel tube walls exhibited a fiber-like structure (Figure 19B & 19D), while the Ca-gel tube walls were too thin to distinguish any features of. The higher pH of the counterion solution in the Ca-gel system is likely to give more amorphous and gelatinous structures.[201,243] Together with the higher growth rate of the tubes, this would stretch the semipermeable membrane created during the growth much more than in the P-gel system, leading to thinner, less crystalline walls. Furthermore, the tubes in both hydrogel systems were slightly heterogeneous (as suggested by the photographs in Figure 14, Section 5.3.3), which could explain some of the variations observed in the SEM micrographs.

The exterior regions of both the Ca-gel and P-gel tubes exhibited two main kinds of structural units, a granular and a needle-like. The granular structure was also found on the interior of both kinds of tubes but is smaller for the Ca-gel tubes. For the P-gel tubes, the interior also exhibited needle-like structures on top of the granules, but these were longer and wider than those observed on the exterior surfaces.

5.4.2. Chemical analysis

Elemental mapping of the tubes was done using EDS, with the main aim of trying to assess the possible presence of κ-carrageenan in the structures. The analysis was done in three regions of the 1-day (II) P-gel tubes and four regions of the 3 h (II) Ca-gel tubes, 1-day (III) Ca-gel tubes and 1-day (III) P-gel tubes. The samples were chosen to give as comparable samples as possible between the two studies. The analyzed regions are assigned in Figure 21 and Figure 22.

The element mapping showed relatively similar chemical composition for both 1 day (II) P-gel and 3 h (II) Ca-gel tubes at the regions 1, 2, and 3 where the main elements are Ca, P, and O (Figure 21). Table 11 summarizes the atom percentage (%) of the four main elements (Ca, P, O, and C) at different regions of the walls of the tube of **Paper II**, calculated from the EDS spectra of Figure 21. This is indirect evidence that both tubes are formed by CaP. Unlike the 1-day (II) P-gel tube, the 3 h (II) Ca-gel tube possesses an extra layer, that can be seen in region 4 in Figure 21B, where an intensive signal of C is found, indicating the likely presence of κ-carrageenan. The signals from Na and Cl found in 3 h (II) Ca-gel tube and 1-day (II) P-gel tube respectively, are believed to be from the counterion solutions.

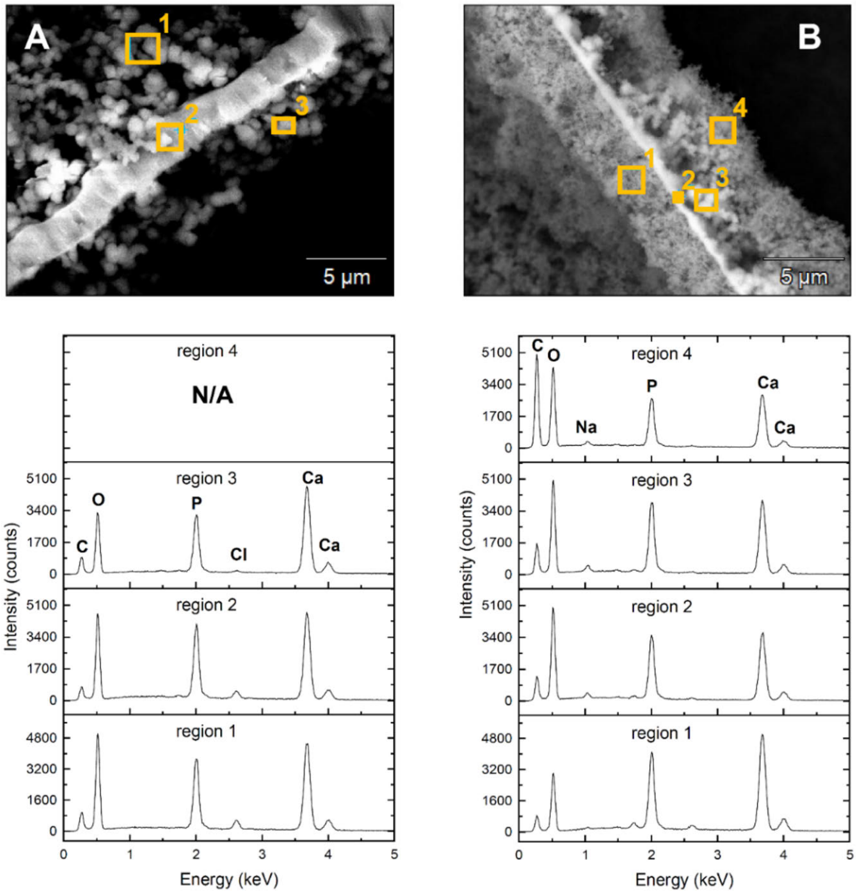
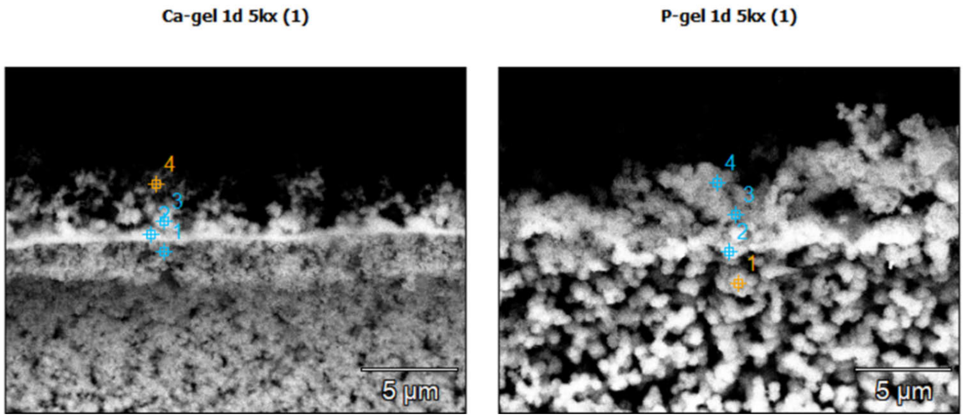


*Figure 21. Cross-section of P-gel 1-day (II) and Ca-gel 3 h (II) tubes and EDS spectra taken from different regions (indicated by orange boxes) of the tube walls. [Figure 2, **Paper II**].*



Ca-gel 1d 5kx (1)

P-gel 1d 5kx (1)

Figure 22. Regions chosen for the EDS analysis as seen from the 1-day (III) Ca-gel sample (left) and 1-day (III) P-gel sample (right) in 5k magnification. [Figure S6, ***Paper III****].*

The atom percentages of all the investigated samples are presented in Table 11 (Ca-gel 3 h (II) and P-gel 1-day (II)) and Table 12 (Ca-gel 1-day (III) and P-gel 1-day (III)). An interesting finding of the elemental mapping of the tubes in **Paper III** was the presence of sulfur, which is a strong indication of the presence of κ-carrageenan in the structure.

Table 11. Atom percentages (%) of the four main elements (Ca, P, O, C) at different regions of the tube walls of the P-gel 1-day (II) and Ca-gel 3 h (II) samples, calculated from the EDS spectra found in Figure 21 [Table S3, ***Paper II****]*

Atom	**Percentage at the region**							
	1		**2**		**3**		**4**	
	P-gel	*Ca-gel*	*P-gel*	*Ca-gel*	*P-gel*	*Ca-gel*	*P-gel*	*Ca-gel*
Ca	13.41	15.96	14.84	9.19	17.21	9.07	n.a	5.51
P	7.20	8.45	8.22	6.19	7.64	6.16	n.a	3.48
O	63.76	57.36	63.93	61.63	58.40	58.99	n.a	42.85
C	14.65	16.83	11.93	21.80	16.27	24.50	n.a.	47.55

Table 12. Atom percentages (%) for the tubes in ***Paper III*** *arranged according to the measurement regions, sulfur shown in bold. [Table S3,* ***Paper III****]*

Region 1								
	Ca-gel 1 d	*P-gel 1 d*	Ca-gel 7 d	*P-gel 7 d*	Ca-gel 14 d	*P-gel 14 d*	Ca-gel 28 d	*P-gel 28 d*
C	26.31	*16.05*	11.93	*9.34*	20.20	*10.45*	15.25	*8.91*
O	53.77	*65.52*	62.64	*65.59*	56.77	*67.83*	67.25	*63.06*
Ca	12.34	*11.70*	15.38	*16.30*	39.80	*14.03*	10.04	*18.51*
P	6.75	*6.65*	8.54	*8.39*	42.30	*7.46*	5.88	*8.81*
S			**0.02**		**0.04**			
Region 2								
	Ca-gel 1 d	*P-gel 1 d*	Ca-gel 7 d	*P-gel 7 d*	Ca-gel 14 d	*P-gel 14 d*	Ca-gel 28 d	*P-gel 28 d*
C	25.32	*30.28*	12.60	*14.67*	24.21	*9.47*	14.54	*41.94*
O	50.95	*53.00*	64.35	*64.44*	57.07	*67.11*	64.38	*41.82*
Ca	14.73	*11.09*	11.63	*13.46*	10.61	*15.25*	11.95	*11.17*
P	8.10	*5.54*	7.84	*6.99*	5.52	*7.74*	6.94	*4.81*
S			**0.03**		**0.02**			
Region 3								
	Ca-gel 1 d	*P-gel 1 d*	Ca-gel 7 d	*P-gel 7 d*	Ca-gel 14 d	*P-gel 14 d*	Ca-gel 28 d	*P-gel 28 d*
C	16.94	*37.06*	17.69	*40.26*	28.96	*12.70*	16.02	*52.61*
O	60.55	*40.17*	59.82	*46.28*	39.80	*65.62*	57.84	*35.25*
Ca	13.29	*15.63*	10.11	*8.93*	18.08	*14.37*	14.52	*8.14*
P	8.14	*6.92*	7.67	*4.20*	10.26	*6.89*	8.95	*3.70*
S								

Region 4								
	Ca-gel 1 d	*P-gel 1 d*	Ca-gel 7 d	*P-gel 7 d*	Ca-gel 14 d	*P-gel 14 d*	Ca-gel 28 d	*P-gel 28 d*
C	23.28	*38.49*	28.89	*43.65*	35.43	*15.03*	27.68	*80.69*
O	57.98	*44.52*	54.04	*47.23*	42.30	*65.55*	49.95	*18.62*
Ca	11.04	*11.41*	10.11	*6.13*	18.08	*12.78*	12.86	*0.51*
P	6.78	*5.38*	5.45	*2.80*	7.32	*6.30*	7.54	*0.18*
S								

5.4.3. Structural properties

Further, to investigate the difference between the Ca-gel and the P-gel systems, the tubes were characterized using XRD. The XRD patterns of the 1-day (II) P-gel tubes and 3 h (II) Ca-gel tubes, as well as patterns for the sample holder and the neat κ-carrageenan are found in Figure 23.

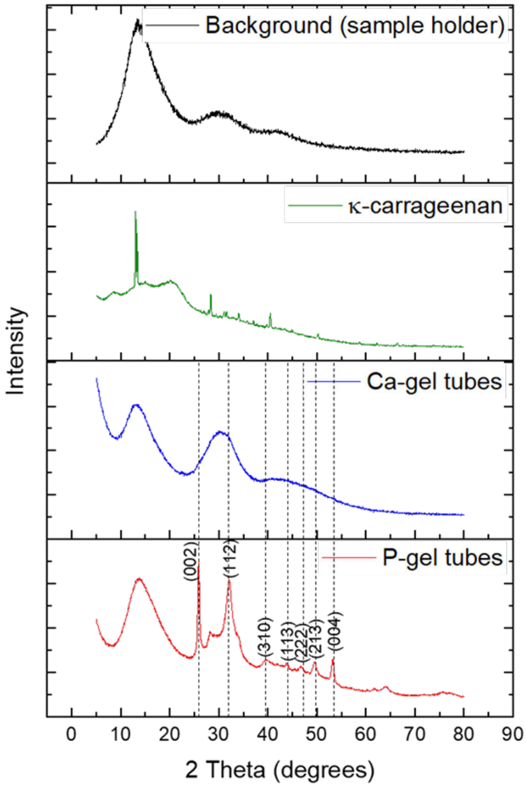


*Figure 23. XRD patterns of Ca-gel 3h (II) and P-gel 1-day (II) samples, as well as the neat κ-carrageenan powder and background (sample holder). [Figure S6, **Paper II**].*

Due to the small amounts of the collected samples, a strong background signal from our sample holder was present for both samples (broad peak at around 12°). However, Figure 23 can still expose the XRD patterns of two different kinds of tubes. The 3 h (II) Ca-gel sample is amorphous and shows no sign of being crystalline. This is also validated by that after evaporation of the washing ethanol, the tubes have lost their form and turned to powder, which did not occur for the P-gel tubes. The XRD pattern showed one broad peak in addition to the one from the sample holder (12°), found at 30°. This one is in agreeance with the pattern of ACP, that exhibits a broader hump with its maximum at ca 30°.[244] A contributing factor for the lack of crystalline material in the Ca-gel tubes could be the very short amount of time the tubes were kept in the counterion solution. For example, Hughes et al.[200] and Kim et al.[215] report changes in the diffraction patterns with time. Figure 23 also includes the diffraction pattern for the 1-day (II) tubes from the P-gel system. The shape of the non-flat baseline could be from the background or due to a partly amorphous sample. When comparing the graphs against known patterns, we have looked at the peaks at approximately 26°, 28°, 32°, 39.5°, 44°, 47°, 49.5°, 53°, 62°, 64.5° and 75°, which match closely against HA (JCPDS #00-046-0905).[245] The difference in crystallinity might also be explained by the differences in pH of the solutions in which the tubular growth takes place. A higher pH is likely to give a more amorphous material.[243] In addition, not only are the Ca-gel tubes in solution for a much shorter period but the growth itself is also very rapid in comparison to that of the P-gel tubes. Both the pH and time spent in solution[246] likely play a part of the resulting difference in the crystallinity.

The lack of crystallinity in the 3 h (II) Ca-gel tubes was one of the main reasons for investigating the maturation process in **Paper III**. For these measurements, the sample holder used in **Paper II** was exchanged for a glass slide with double-sided tape (Figure 24). The obtained PXRD patterns for the tubes of **Paper III** can be found in Figure 25.

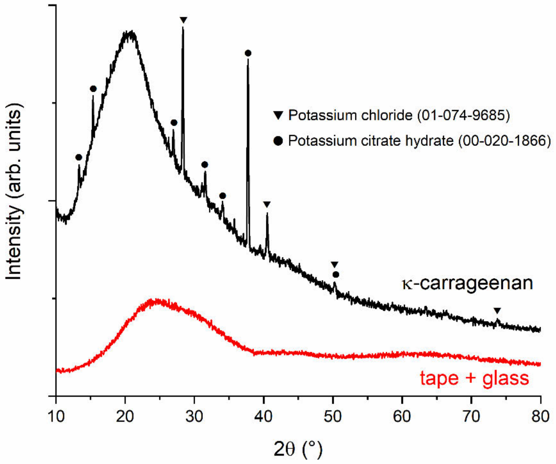


*Figure 24. XRD-patterns of the κ-carrageenan powder used in the experiments and the tape and glass slide used for the XRD samples during measurements. [Figure S5, **Paper III**].*

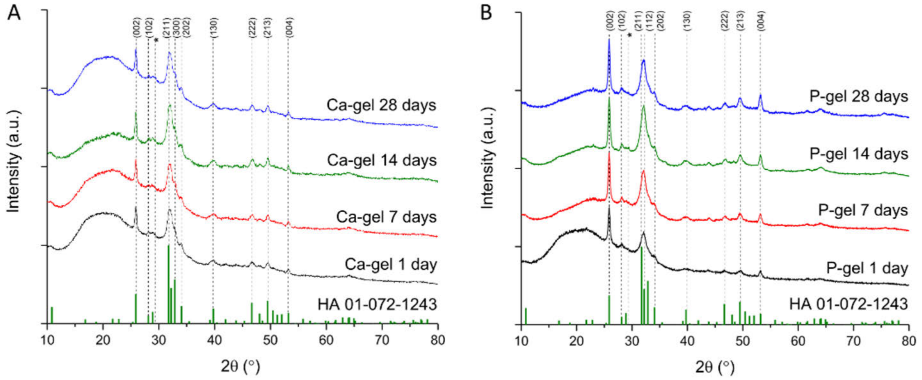


*Figure 25. XRD patterns of Ca-gel (III) tubes (A) and P-gel (III) tubes (B). [Figure 5, **Paper III**].*

The most prominent peaks in the XRD patterns of the **Paper III** tubes were found at 25.9° and ~32°, where the second peak consists of several reflections combined. The XRD data of all samples matches well with the reference pattern of HA (JCPDS #01-072-1243). However, it should be noted that also CDHA (JCPDS #00-46-0905) would give an almost identical XRD pattern. Even though the dominating forms of phosphate are PO_4^{3-} at pH 13 and HPO_4^{2-} at pH 11 (see Figure 13, Section 5.3.2) in the counter solutions of Ca-gel and P-gel systems, respectively[247], HA is the main precipitation product which could be explained using the predominance area diagram of CaPs[248]. In addition, a broad hump at 12–35° was visible for the samples having spent less time in the counterion solution, and it was also more evident for the Ca-gel samples compared to the P-gel samples. This hump can either be attributed to κ-carrageenan (Figure 24), the sample holder (Figure 24), ACP[244], or a combination of these. The presence of κ-carrageenan in some of the tubes was also indicated by trace amounts of sulfur, which could be found in the 7-days and 14-days Ca-gel tubes according to the EDS data (Table 14).

While the peaks in the XRD patterns for both P-gel (III) tubes and Ca-gel (III) tubes appeared at the same angles when comparing the samples of the two systems, the relative intensities of the two highest ones (at 25.9° and 32°) differ. This indicates a difference in the preferred orientation of the crystal structure for the P-gel tubes, seen as pronounced reflections at 25.9°, 32.2° and 53.2°, corresponding to the (002), (112) and (004) reflections of HA. The (002) and (004) reflections can be attributed to a layered structure as the planar growth directions would result in a similar reflection enhancement. This was supported by the SEM micrographs (Figure 19C, 19D), where the P-gel (III) tubes had a distinctively thicker wall consisting of a fiber-like structures.

The more mature samples of both the Ca-gel (III) tubes (14- and 28-days) and P-gel (III) tubes (7-, 14- and 28-days) had additional peaks at 29.4° (indicated with an asterisk in Figure 26), 39.4° and 43.1° that fit well with the pattern for calcite ($CaCO_3$, JCPDS #00-005-0586). These peaks were most clearly visible in the 14 days P-gel (III) sample and 28 days Ca-gel (III) sample (P-gel sample also had visible peaks at 23.0° and 36.0° that fit with the calcite pattern). When analyzing the structures appearing on the surface of the Ca-gel counterion solution (Figure 15, Section 5.3.3), the intensity of these calcite peaks was even more evident (Figure 26). As the peaks are most intense in the structure on the surface of the counterion solution, we expect that the calcite formation is due to carbon dioxide from the air dissolving into the solutions. In addition, the source of carbonate cannot be from carrageenan as there is no relevant compound found in the XRD pattern of carrageenan (Figure 24).

The gradual change observed in our XRD patterns, especially the peaks around 50–55° of the P-gel tubes, is consistent with crystallization of HA, shown for example by Rollin-Martinet et al..[249] However, both HA and CDHA are usually poorly crystalline when unsintered.[203] In addition, ACP tends to slowly recrystallize into compounds with better crystallinity such as CDHA when left in its parent solution.[203,244] It is possible that this process is slowed down further in our case since one of the required ions is initially locked inside the gel (especially in the case of the Ca-gel system). Overall, the P-gel tubes seem to have a more crystalline structure than the Ca-gel tubes.

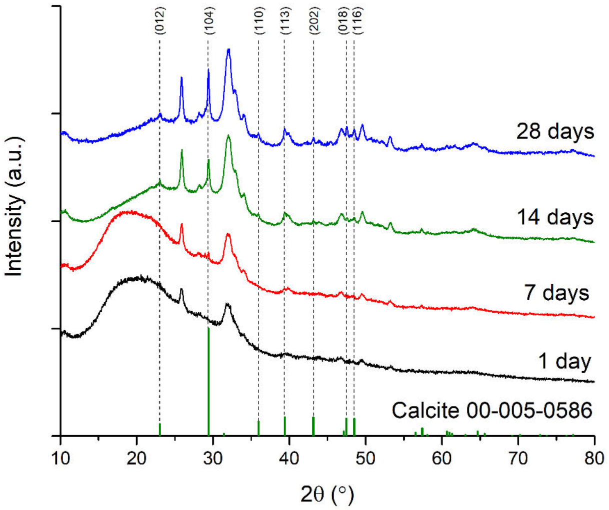


Figure 26. Obtained XRD patterns for the layer forming on the surface of the Ca-gel counterion solution with the XRD pattern of calcite for reference. [Figure S7, ***Paper III****]*

5.4.4. Thermal behavior

The thermal behavior was investigated for both types of 1.5 wt% tubes in **Paper II** and all tubes as well as the Ca-gel system surface layer in **Paper III**.

Thermogravimetric analysis data of the samples from **Paper II** are shown in Figure 27 and from **Paper III** in Figure 28. The samples in **Paper II** were analyzed in the temperature interval of 30 to 600 °C and a heating rate of 10 °C/min. In **Paper III** the samples were analyzed in the temperature interval of 30 to 1000 °C and a heating rate of 5 °C/min. As references in **Paper III**, analysis was also done on the neat κ-carrageenan powder and the top layer formed on the Ca-gel counterion solution after 1 day and 28 days (Figure 29).

The Ca-gel 3 h (II) sample showed two larger stages of mass loss while the P-gel 1 day sample showed only one (Figure 27). All the Ca-gel (III) and P-gel (III) samples showed three larger stages of mass loss (Figure 28). All samples exhibited a gradual mass loss below 200 °C, corresponding to the loss of physisorbed water.[250] Amorphous 3 h (II) Ca-gel tubes had a greater water weight loss (10.16%) comparing to the more crystalline 1-day (II) P-gel tubes with a water weight loss of 8.10%. The mass loss was also greater for the Ca-gel (III) samples (8.2–9.7 %) comparing to the P-gel (III) samples, where the 1-day P-gel sample (7.9 %) showed significantly more mass loss than the rest of the P-gel samples (5.6–6.1 %). This was consistent with the phase structures of the materials since amorphous structures have higher surface areas where the physisorption can take place.[213,250] Thus, the amount of physisorbed water decreases with a higher degree of crystallinity of the material. These results are in line with the observations on sample crystallinity from the XRD patterns (Figure 23, Figure 25).

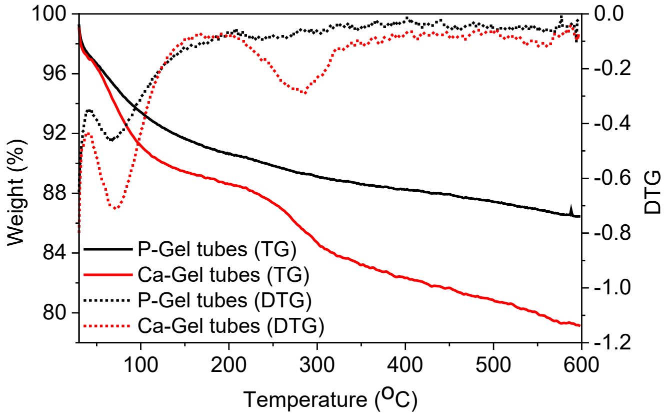


*Figure 27. TG and DTG curves of Ca-gel 3 h (II) tubes and P-gel 1-day (II) tubes. [Figure S7, **Paper II**]*

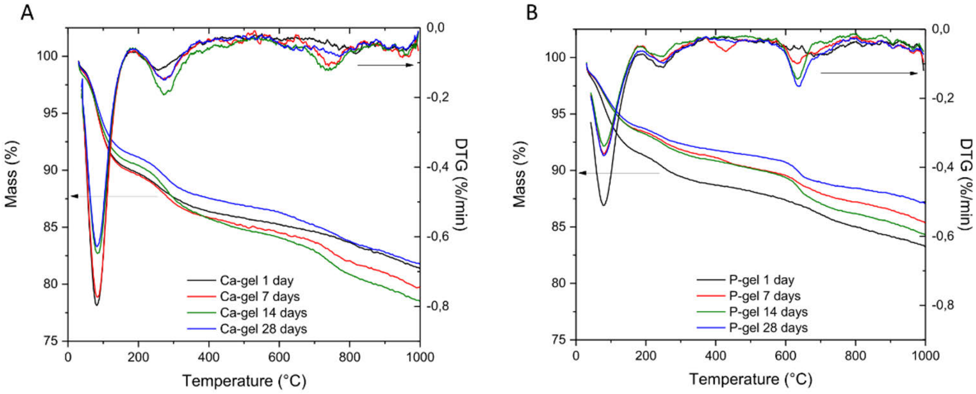


*Figure 28. TG and DTG curves from for Ca-gel samples (A) and P-gel samples (B), showing measurements of 1- (black), 7- (red), 14- (green), and 28-day (blue) samples. [Figure 6, **Paper III**]*

A second mass-loss step was observed for all the (III) samples between 180–330 °C (Figure 28). In this temperature range, the mass loss for the Ca-gel (III) samples (2.6–3.6 %) is larger and more pronounced than for the P-gel (III) samples (1.2–1.8 %), where a clear decrease is visible especially for the 14-day Ca-gel sample (3.6 %). The mass loss in this region corresponds to loss of structural water (between 200–400 °C), but also decomposition of organic molecules like polysaccharides (starting from 200 °C).[213,250,251] In the case of the Ca-gel (III) samples, the behavior above 250 °C resembled that of the neat κ-carrageenan powder (Figure 29). The same behavior is observed at around 250-286 °C for the Ca-gel (II) sample. The slight shift of the mass loss of the Ca-gel (III) samples towards higher temperature when compared to that of the neat κ-carrageenan can be attributed to the interaction of κ-carrageenan and CaP due to the formation of hydrogen bonds between HA and the sulfonic groups of κ-carrageenan, giving an increase in thermal stability.[213,214]

The tubes in **Paper II** were not analyzed above 600 °C, but the P-gel (III) tubes had a third stage of mass loss between 600–660 °C (except for the 1-day grown tubes) and the Ca-gel (III) tubes between 690–780 °C (Figure 28). Between 600–800 °C events such as further decomposition of κ-carrageenan, decomposition of calcium carbonate, volatilization of carbonate ions or decarbonation of CO_3AP take place.[227,252–254] The mass loss observed for the P-gel systems corresponds to the loss of carbonate and correlates well with the presence of calcite peaks in the XRD patterns (Figure 25). The 14- and 28-day Ca-gel (III) samples showed minor mass loss in this region. This behavior is also supported by the thermal behavior of the 28-day Ca-gel top layer (III) sample (Figure 29), where clear calcite peaks could also be observed in the XRD pattern (Figure 26). The mass loss step for the Ca-gel samples between 690 and 780 °C (which was not present in any of the P-gel samples), corresponds to the further decomposition of κ-carrageenan. A resemblance to this behavior can be seen in the mass loss of the neat κ-carrageenan (Figure 29), albeit with a shift to higher temperatures due to the stabilizing interaction of the HA in Ca-gel samples. The obtained EDS data (Table 12) confirmed traces of sulfur (found in κ-carrageenan) in the 7 days and 14 days Ca-gel (III) samples. This suggests that these two samples contained more κ-carrageenan than the other samples, which is in line with the fact that these two samples exhibit the largest mass loss in this temperature range.

TG and DTG curves of the neat κ-carrageenan powder used in the hydrogels, as well as of the top layer formed on the Ca-gel counterion solution (Figure 15) after 1 day and 28 days are shown in Figure 29. The top layer of the Ca-gel solution showed a larger mass loss step between 600–750 °C. The neat κ-carrageenan showed five distinct stages of mass loss in the temperature ranges 40–120 °C, 160–210 °C, 210–290 °C, 290–550 °C, and 660–750 °C.

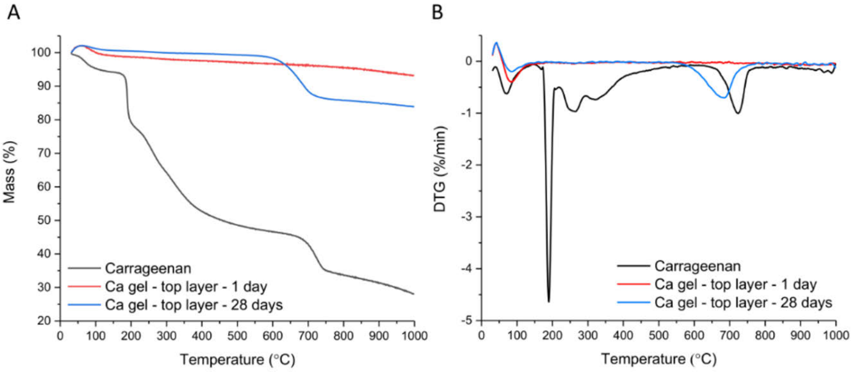


*Figure 29. TG (A) and DTG (B) curves of the neat κ-carrageenan powder (black), 1 day-sample of Ca-gel top layer (red) and 28 days-sample of Ca-gel top layer (blue). [Figure S8, **Paper III**]*

*Table 13. Mass losses in the peak regions of the DTG curves (Figure 6). DTGmax gives the temperature for the maximum of the peak of that specific region. [Table S4, **Paper III**]*

Ca-gel, mass loss				
Sample	**Region 1, 30–180 °C (DTG$_{max}$)**	**Region 2, 180–330 °C (DTG$_{max}$)**	**Region 3, 690–780 °C (DTG$_{max}$)**	**Total**
1 day	10.0 %, (79 °C)	2.6 %, (256 °C)	0.9 %, (777 °C)	18.6 %
7 days	10.2 %, (83 °C)	3.0 %, (265 °C)	1.7 %, (766 °C)	20.3 %
14 days	9.4 %, (83 °C)	3.6 %, (276 °C)	2.1 %, (758 °C)	21.5 %
28 days	8.6 %, (81 °C)	2.9 %, (284 °C)	1.4 %, (767 °C)	18.2 %
P-gel, mass loss				
Sample	**Region 1, 30–180 °C (DTG$_{max}$)**	**Region 2, 180–330 °C (DTG$_{max}$)**	**Region 3, 600–660 °C (DTG$_{max}$)**	**Total**
1 day	8.5 %, (79 °C)	1.8 %, (246 °C)	0.5 %, (620 °C)	16.8 %
7 days	6.4 %, (79 °C)	1.5 %, (250 °C)	0.8 %, (627 °C)	14.7 %
14 days	6.6 %, (79 °C)	1.6 %, (250 °C)	1.1 %, (640 °C)	15.7 %
28 days	6.2 %, (78 °C)	1.2 %, (254 °C)	0.9 %, (637 °C)	12.9 %

5.5. Limitations of the study

The study of the developed outreach and teaching materials suffered from the COVID-19 pandemic. The sample of 33 students for the writing board was quite small and the questionnaire used was originally intended to be used just as preliminary evaluation, before doing a revision of both the concept and the questionnaire, followed by a more thorough study. There was also no possibility to try out the chemical garden outreach concept in any form, and therefore it remains a suggestion even though the teaching aspect was an important factor during the conceptualization of the study. No validated questionnaire was used, and no follow-up study was made. The results do not give any indications as to how well it really worked in increasing any interest.

For the chemical garden structures, characterization with Raman spectroscopy and thermal treatment followed by XRD would have given useful information of the CaP phases present. Based on the present data no certain distinction could be made between HA and CDHA phases.

The use of the commercial κ-carrageenan throughout the thesis was a deliberate choice and a big part of the approach of the study. This did not affect things such as repeatability, yet it should be considered that the use of purer κ-carrageenan might have an effect on the grown structures.

6. CONCLUSIONS

The results reported within this thesis show that it is possible to utilize commercial κ-carrageenan to create both new materials for chemistry teaching and outreach as well as chemical garden structures. The results also show that all of these can be produced with such simple methods and materials, that these studies are possible to re-create within an outreach or classroom setting.

The κ-carrageenan was used to create a pH sensitive hydrogel writing board that can be used for teaching topics such as acid-base chemistry, redox reactions and electrochemistry. In addition to κ-carrageenan, easily accessible items and chemical such as Epsom salt, red cabbage, bilberries, 9V batteries and copper wire, all accessible from the grocery and hardware store was used. The result of the limited questionnaire with upper secondary students (N=33) evaluating the concept indicates that the experiment was appreciated, triggered a situational interest in the participating students. Additionally, we also observed that the students enjoyed the writing board and especially the creative freedom and artistic elements of the experiment. Further, the experiment is easily scalable for both different kinds of groups and settings as it is safe, does not require fancy/expensive equipment and does not produce hazardous waste. Additionally, all aspects of the experiment (including hydrogel preparation) can be done practically anywhere, also by students. The use of the hydrogel plays the biggest part in updating old, classic experiments to new and innovative standards.

The emphasis of the studies on chemical gardens was to compare two systems that were inverted in reference to one another regarding the two precipitate forming ions (Ca^{2+} and PO_4^{3-}). The initial aim was to keep the parameters in the preparations of both systems as equal as possible. Both created systems were successful as such. The two systems were, however, too different from each other for the equality to be entirely achievable. The main similarities between the systems in the end was the amount of κ-carrageenan used in the hydrogels of the tubes that were compared and the use of the same ions. Future studies and optimizations would therefore benefit from being done separately for each system.

The created systems were used to investigate not only the difference between the tubes of the two systems, but also the influence of the hydrogel stiffness and a longer maturation time of the tubes in their parent counterion solution. The different characterization methods showed differences in properties of the tubes, such as length, diameter, macrostructure, wall size and the structure (SEM), crystalline phases (XRD) and in the thermal decomposition (TG and DTG).

Structures grown from the Ca-gel system grew tall and in a completely straight formation, but with a very thin wall. Characterizations showed that the tubes kept in solution for only 3 hours were amorphous, while the tubes kept for at least one day showed phases of HA/CDHA. Tubes kept in solution for at least 14 days also showed traces of calcite in the structure. Additionally, the Ca-gel tubes showed clear indications of containing κ-carrageenan, making them a potential candidate for future composite studies.

Structures grown from the P-gel system were shorter, more kinked but also more rigid with a thicker wall. Characterizations showed that all tubes showed phases of HA/CDHA and that they were more crystalline than the Ca-gel samples. For the P-gel samples, tubes kept in solution for at least 7 days also showed traces of calcite in the structure. However, no strong indications of κ-carrageenan within the structure could be found.

Unfortunately, with the methods used in this thesis it was not possible to tell whether the tubes contained hydroxyapatite or calcium-deficient hydroxyapatite.

No indications of impurities due to the use of commercial κ-carrageenan were found in the tubes during characterization and the CaP phases were in line with what could be expected when comparing with the results of others. Future studies will tell whether there are big differences between tubes grown from commercial κ-carrageenan hydrogels or those made using purer chemicals. One important factor with the commercial κ-carrageenan is that it is very easy to work with, which should be regarded as a huge advantage in relation to the scope of this thesis: making the methods easily accessible and easy to work with. This allowed the tubes to be used within an art exhibition where the systems could be made on site, thereby reducing unnecessary problems with transport of ready systems.

Further, the chemical garden systems presented in this thesis where also successfully developed in such a way that it is possible to use these as such for outreach activities, during school visits to campus or in the classroom. This work therefore also shows that it is possible to developed methods that can be used for both research and teaching. This opens a door for bringing research closer to students below university level by involving them in actual research with small means.

7. FUTURE WORK

The hydrogel writing board can still be developed further and used in new settings. The outreach concept of the chemical garden system could not be evaluated, it is however developed to fit this purpose and ready to use. Additionally, the strategic research profiles Technologies for a Sustainable Future and Solutions for Health at the Faculty of Science and Engineering both have research with excellent potential to be incorporated into a larger and more extensive concept in which research opportunities would be offered to upper secondary school students. This could further inspire them to pursue a career in STEM.

The work presented here is only a scratch on the surface regarding the use of κ-carrageenan hydrogels for chemical gardens. For the CaP systems, there is still much room for improvement when it comes to things such as the number of tubes grown from each batch as well as the properties of tubes. In this thesis, the κ-carrageenan played the main role, and therefore we have only used the added amount of κ-carrageenan and the placing in the system of the precipitating ions to control the growth.

So far, no investigations have been done on thermal treatment or mechanical properties. Many opportunities for controlling tubular properties lie within further investigations of parameters such as concentrations, pH and salts used in both the layering solution and hydrogels as well as the quality of the κ-carrageenan used, as for example concentration of the layering solution has been shown to affect the microstructure. The Ca-gel system also seemed to give tubes with some amount of κ-carrageenan incorporated in the structure, suggesting the possibility of growing composites. Finally, the studies of chemical garden systems using κ-carrageenan can hopefully be extended to include structures of other compositions in the future.

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APPENDICES

Appendix 1. Lab work for outreach - Writing board

Introduction

In this lab we will be performing electrolysis if water, but in a slightly different way than you might have expected. This will be performed in a gel containing water, salt and red cabbage juice.

Electrolysis is a technique that uses a direct electric current (DC) to drive an otherwise non-spontaneous chemical reaction.

During the electrolysis of water the following reactions occur:
At the anode (+): $2\ H_2O\ (l) \rightarrow\ O_2(g) + 4\ H^+\ (aq) + 4\ e^-$
At the cathode (-): $4\ H_2O\ (l) + 4\ e^-\ \rightarrow 2\ H_2\ (g) + 4\ OH^-\ (aq)$

Below you can see all the different colours that red cabbage juice can take at different pH.

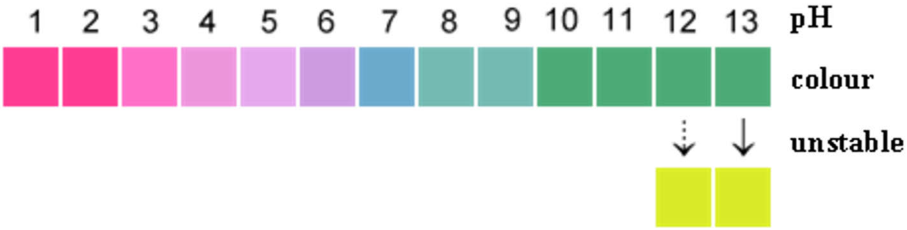

Figure 1. The colours of red cabbage at different pH values (http://chem-www4.ad.umu.se:8081/Skolkemi/rodkal.html).

Instructions

Materials

- Petri dish with red cabbage gel and (copper wire)
- 9 V battery
- Two wires with alligator clips
- Pen (with copper wire), you write with the bent part

Using the information given in the introduction, can you write your name in the gel ***in a way that making scratches is not your primary form of writing***? Some scratches are inevitable, but you should avoid them as much as possible.

I recommend you start testing your set up by writing in the outer regions of your gel.

- How many colours can you produce?
- Can you tell which terminal of the battery you have used for writing?

Appendix 2. Lab work for classroom – writing board

Introduction

In this lab work, we will be writing using electrochemistry and electrolysis of water, this will be performed in a gel containing water, salt and red cabbage juice. Before starting with the experiment, there are a few facts you need to know and some questions for you to consider.

Fact 1. Electrolysis is a technique that uses a direct electric current (DC) to drive an otherwise non-spontaneous chemical reaction, this is utilized for example in the production of aluminium.

Question 1.

What kind of circuit do you need if you want electricity to flow?

Fact 2. During the electrolysis of water the following reactions occur:
At the anode (+): $2\ H_2O\ (l) \rightarrow\ O_2(g) + 4\ H^+\ (aq) + 4\ e^-$ (1)
At the cathode (-): $4\ H_2O\ (l) + 4\ e^-\ \rightarrow 2\ H_2\ (g) + 4\ OH^-\ (aq)$ (2)

Question 2.

Identify all the different species that are present in equation (1) and (2).

What can you tell about them? In what context have you encountered them before?

Fact 3. Figure 1 (below) illustrates the different colours that red cabbage juice will take at different pH.

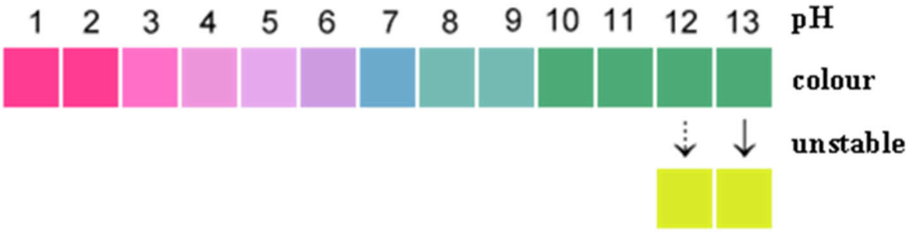

Figure 1. The colours of red cabbage at different pH values (http://chem-www4.ad.umu.se:8081/Skolkemi/rodkal.html).

Question 3.

What colours does red cabbage have at acidic pH?

What colours does red cabbage have at alkaline pH?

Question 4.

Combining your knowledge from question 2 and question 3:

- ***what colour change do you expect at the anode?***
- ***what colour change do you expect at the cathode?***

Instructions

Before you start with anything else in the experiment, you should decide what colour you would like your text to have (see Figure 1).

Using the materials presented in the list below, build a circuit that will allow for the flow of electricity through the gel. You will write with the pen, so depending on our colour of choice: which terminal should you attach the pen to?

Materials

- Petri dish with red cabbage gel and (copper wire)
- 9 V battery
- Two wires with alligator clips
- Pen (with copper wire), you write with the bent part

Once you have created your circuit you are to write your name in the gel. Making scratches in the gel should **not** be your main technique of writing. Gels are usually soft as material, so please treat it carefully. The outermost edges of the gel are a good place to try your writing, there you can also try how much (or little!) pressure you need to use to produce text.

Once you have written your name, try to see how many different colours you can produce in the gel. Is the colour of your text dependent on the time you hold the pen against the gel? Does the colour change when changing the terminal of the battery?

Ideas for further investigations

- Investigate what other kinds of natural indicators you can find in your kitchen or your garden.
- Investigate what other household materials you can use to make a gel.
- Investigate if there are other algae-based materials you can use to make gels.
- Investigate the properties of some commonly used laboratory grade indicators. What are the benefits of using natural indicators instead? What are your thoughts on exchanging the laboratory grade indicators to natural ones?

ORIGINAL PUBLICATIONS

Fogde, A.; Kurtén, B.; Sandberg, T.; Huynh, T.-P. Colorimetric Hydrogel from Natural Indicators: A Tool for Electrochemistry Education. *Journal of Chemical Education.* 2020, 97 (10), 3702–3706.

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Activity

Colorimetric Hydrogel from Natural Indicators: A Tool for Electrochemistry Education

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Cite This: *J. Chem. Educ.* 2020, 97, 3702−3706

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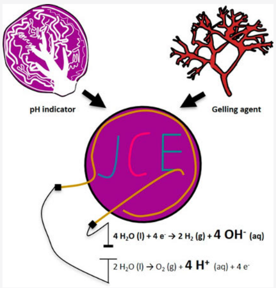
ABSTRACT: The electrolysis of water is popular both as lab work and as a demonstration. In this activity, the electrolysis of water in the presence of a pH indicator is used to produce text and symbols. This report describes the design of an environmentally friendly setup of a writing board utilizing the electrolysis of water in a hydrogel environment. The activity can be performed by only using chemicals and materials that are easily accessible to everyone, with no special permit needed. The writing board has been developed mainly as an outreach activity for our faculty and has been assessed during visits from upper secondary school students.



KEYWORDS: *General Public, High School/Introductory Chemistry, Public Understanding/Outreach, Hands-On Learning/Manipulatives, Acids/Bases, Electrochemistry, Oxidation/Reduction*

■ INTRODUCTION

Electrochemistry is an important subject as it is not only very common in everyday life but also important in our society. Its applications can be found in batteries, accumulators, fuel cells, study of the corrosion process, and industrial-scale production of important metals like aluminum.[1] Some classic experiments and demonstrations on the subject include writing messages and designing art by exploiting the electrolysis of water.[2] Many excellent examples on how to create laboratory work and how to visualize the products using color changes have been published frequently. Some of the examples have used electrolysis of water for demonstrating the chemical composition of water and/or for illustrating the redox reactions using color changes,[3−7] while others have developed microscale laboratory exercises.[8,9]

In the electrolysis of water with an inert electrolyte, half-reactions occur at

$$\text{anode} \quad 2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad (1)$$

$$\text{cathode} \quad 4H_2O(l) + 4e^- \rightarrow 2H_2(g) + 4OH^-(aq) \qquad (2)$$

The electrolytic products including H^+ and OH^- from eqs 1 and 2, respectively, show why pH indicators are a natural choice for illustration of the redox reaction. Examples of indicators used for this purpose include bromocresol green, bromothymol blue, and thymolphthalein.[3,4,6] Another popular natural pH indicator is the juice of red cabbage due to its nontoxicity and broad changes in color. It is commonly used in Finnish schools, especially for the lower grades.[10,11] The reason for the changes in color with pH are anthocyanins, the compounds that are present in red cabbage as well as in blueberries. The anthocyanins in red cabbage will change their color depending on pH of the environment such as a green at highly alkaline, blue at slightly alkaline, purple around neutral, pink at slightly acidic, and red at highly acidic conditions.[11]

Experiments in liquid media often require careful handling and uncontrollable contour of products; thus, gelatin and agar have been used to prepare hydrogels for electrochemistry by both Stauffer and Fox[6] and Davis et al.[8] Another interesting group of compounds for making gels are carrageenans, natural polysaccharides that can be extracted from red algae, some of which can be found also in parts of the Baltic Sea. Carrageenans are common in everyday life as they are used as stabilizers, thickeners, and gelling agents for example in the food industry. Aqueous solutions of carrageenans with specific cations will form physically cross-linked polyelectrolyte gels, that are thermoreversible.[12−14]

In this work, we have combined the teaching of pH and electrochemistry inspired by reported methods from

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others,[2−11] focusing here on showing the wonders of everyday chemistry. In this paper, we describe the design of an environmentally friendly setup of a writing board utilizing the electrolysis of water in a hydrogel environment. The concept of using electrochemistry for producing text has been reported by others.[2,15,16] The emphasis of the method reported in this paper has been on the electrolysis of water with the key factors being a safe and environmental friendly experiment. The reactions both at the cathode and at the anode can be performed without any special equipment, space, or ingredients. The setup has been developed for school visits to our Faculty of Natural Science and Engineering at Åbo Akademi University. Our aim is foremost to introduce chemistry in a fun and surprising way, showing that chemistry is present in our everyday lives and does not have to be dangerous. We have also taken this as an opportunity to show that chemistry does not have to be just test tubes; it is so much more and can also be a form of art. As an additional experiment, we also demonstrate how the hydrogel can be used for making stencil pictures.

■ DESIGN

Materials

Reagent grade K-carrageenan, anhydrous magnesium sulfate, and ammonium hydroxide were acquired from Sigma-Aldrich. Reagent grade hydrochloric acid was acquired from Merck. K-carrageenan (SpecialIngredients) for cooking purposes and Epsom salt (magnesium sulfate, Nortembio) were bought through Amazon but are also available through pharmacies and health food stores. Red cabbage (*Brassica oleraceae*), bilberry (European blueberries, *Vaccinium myrtillus*), vinegar, citric acid, baking soda, and 9 V batteries were all purchased from a local supermarket. Petri dishes (d 90 mm) were acquired from VWR. The copper wire was bought from a local hardware store.

Hazards

All materials used in the writing board experiment are nonhazardous. For the stencil pictures (additional experiment), strong acids and bases are used. Proper lab safety measures should be taken, including working in a fume hood, wearing a lab coat, and using gloves and glasses.

Preparation of pH Indicator Juice

Red cabbage and bilberry juices are chopped and crushed respectively after which newly boiled water (from a water boiler) is poured over and the mixture is left standing for an hour. To remove the solid pieces, the mixture was poured into a flask using a coffee press. For the red cabbage juice, we used 1200 mL of water and 450 g of chopped fresh red cabbage. For the bilberry juice, we used 1200 mL of water and 300 g of frozen bilberries. To have the juice readily available, a large batch can be made and stored in the freezer.

Preparation of the Responsive Hydrogel

To produce the hydrogel, 1.5 wt % of carrageenan is added to a 0.09 M solution of magnesium sulfate consisting of 60% 0.15 M magnesium sulfate solution and 40% indicator juice (prepared as described above). The carrageenan is added slowly and carefully under stirring and heating (70 °C). Care should be taken so that no clots, especially big ones, of carrageenan are formed. The pH of the solution can be adjusted using vinegar, citric acid, or baking soda in order to get the desired color of the gel. When all the carrageenan has been added, the solution can be removed from the heating plate. Upon cooling, the solution forms a hydrogel, and the hydrogel can be stored for more than a week in the fridge.

Preparation of the Writing Board

For writing purposes, the hot (70 °C) solution should be poured into a dish with low edges but a fairly large area (e.g., a Petri dish). The electrode setup for writing includes a ring of copper wire as the anode is placed at the edges of the dish, where one of the ends of the wire as the anode is sticking up so that a battery can be attached using alligator clip wires (Figure 1). The writing is done by attaching the copper wire in the hydrogel to one terminal of a 9 V battery while attaching another piece of straight copper wire (cathode) to the other terminal. We have used the negative terminal for writing as shown in the pictures in Figure 1. The straight copper wire is used as the pen; by making a small bend at the end, one can write by applying it gently and therefore without destroying the hydrogel. We have made copper pens by removing everything but the shell from a ball point pen and sticking the wire through it (Figure 2 and Figure S2, Supporting Information); detailed instructions can be found in the Supporting Information. The hydrogel can be used after a few hours but will work much better if left overnight at room temperature. The firmer the hydrogel is, the better the writing will be. If care

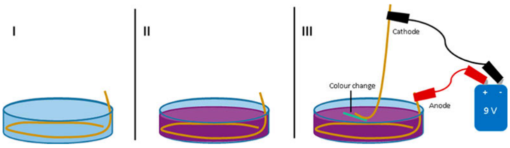

Figure 1. Schematic three-step assembly and use of the writing board: (I) copper wire and Petri dish, (II) copper wire and pH indicator gel in Petri dish, and (III) final assembly of the writing board, with copper wire used as a writing tool attached to the negative terminal of the battery and copper wire in the gel attached to the positive terminal.

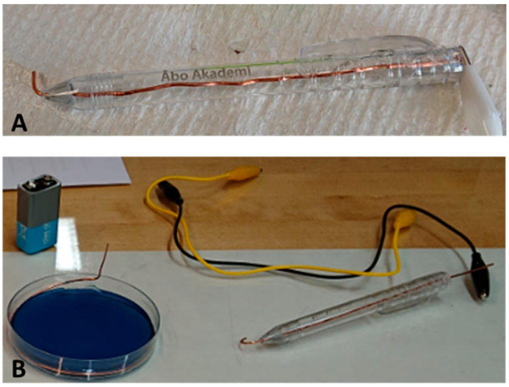

Figure 2. (A) Design of our copper pen used as the tools for writing by visiting students, in the picture attached to an alligator clip. (B) The setup of the experiment as introduced to the visiting students (9 V battery, copper pen, alligator clips, pH indicator gel with copper wire).

is taken not to overheat the hydrogel, it can be reused after careful heating and stirring.

EXPERIMENTAL PROCEDURES

Writing Board Experiment

As mentioned in the Introduction, we have used our writing board when presenting the subject of chemistry at Åbo Akademi University to visiting upper secondary school students. The concept of the writing board has been introduced to the students as a challenge with three tasks:

- Can you write your name in the hydrogel in such a way that scratching the gel is not your main form of producing the letters?
- How many different colors can you produce in the hydrogel?
- Can you tell which terminal of the battery you have used for writing?

The clues given for the task are eqs 1 and 2, and a colored pH scale for red cabbage juice along with a list of the materials available. For the purpose of the last task, the terminals of the battery are hidden beneath duct tape. A more detailed description can be found in Figure 2. Figure 3 and Figure S3 (Supporting Information) shows text produced using the negative terminal of the battery.

Additional Experiments with the pH Responsive Hydrogel

Our main purpose for the hydrogel is using it as the presented writing board. Where electrochemistry has been used by others for writing messages, the pH reactivity of red cabbage has been used to make art in the form of patterns and paintings.[17,18] To add to the versatility of the hydrogel, we have also used it as a substrate for making stencil pictures by exposing it to gases; examples of stencil pictures can be seen in Figure 4. The stencils used for the pictures presented here were made using parafilm. Using the stencils, the hydrogel was exposed to acidic or basic gases according to the desired color. For the included examples, we have used hydrochloric acid (red) and ammonia (green/yellow) (see also Figures S4 and S5, Supporting Information). The stencils can be made by students, but the gas exposure, which must be done in a fume hood, should be left to the teacher and only after taking proper safety precautions. The hydrogels should also be left in the fume hood for a while after the exposure. Since we have a hydrogel, the gases will easily penetrate and dissolve into the hydrogel, causing the color change. The ability to absorb additionally added water is not as good or as fast as that of paper. Therefore, you will not have results that are as nice by trying to paint with acid–base solutions. However, it gives instructors the opportunity to introduce another type of technique.

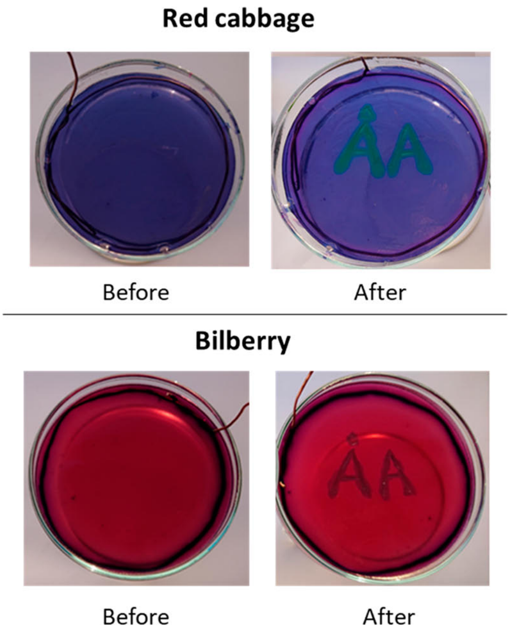

Figure 3. Red cabbage and bilberry hydrogels before and after writing “ÅA” using electrolysis.

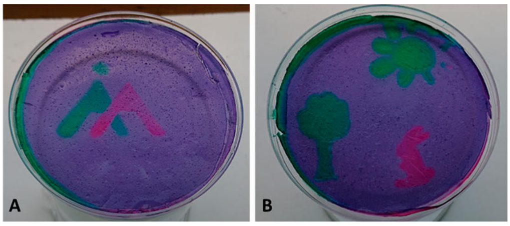

Figure 4. Pictures of (A) letters “ÅA” and (B) random art made using stencils and exposure to hydrochloric acid (resulting red color) and ammonia (resulting green color) gases.

INTEGRATING THE ACTIVITY INTO THE CURRICULUM

This activity can be part of an outreach activity and can also be integrated in the classroom on different levels as it combines many different concepts, for example, acids/bases, indicators, and electrochemistry. The concepts dealt with in the lab work make it suitable for both lower and upper secondary school in accordance with the Finnish curriculum for chemistry education. Something that is also highlighted in the Finnish curriculum is the importance of building a sustainable future, as this lab work builds on the ideas of biodegradability and fits well also with this important subject.

EVALUATION

The experiment has been tested with 33 students from three different schools. After being introduced to the concept and finishing the three tasks mentioned earlier, the students were asked to evaluate their experience with the writing board. The students were asked about their earlier experiences with the electrolysis of water and about their opinions regarding the use of the writing board. Some questions had been left unanswered by some of the students, and some had filled in the form as a pair. The survey of their earlier experience with electrolysis of water was evaluated with yes or no questions. The survey regarding their opinions of working with the board was evaluated using open questions. The results of the survey can be found in Figure 5A,B, where the answers to these open questions could all be categorized as being either “yes” or “somewhat”. Some answers to the question “Other comments?” can be found in Box 1.

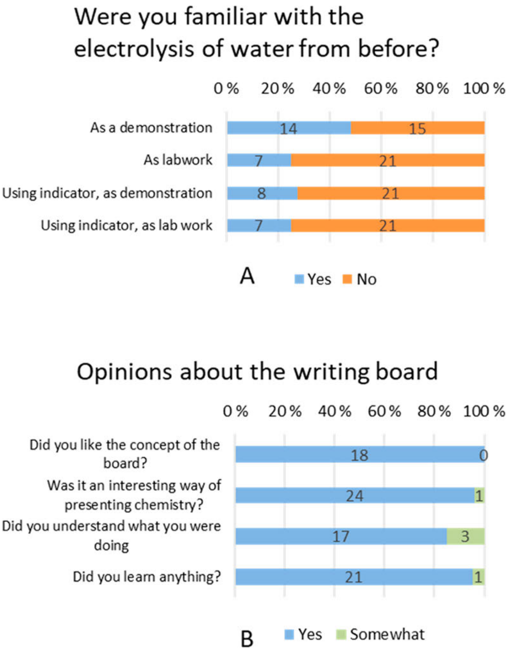

Figure 5. Results of the questions regarding (A) earlier experience of the electrolysis of water and (B) the open questions about the experience of using the writing board.

Box 1. Examples of Comments Given by Visiting Students

- “it was fun”
- “it was a very interesting technique”,
- “it was a good way of making it interesting”
- “I don’t like chemistry at all but this was a good way to make it interesting”

■ DISCUSSION

There are multiple reasons regarding why we have chosen to use natural pH indicators and carrageenan. One of them is the opportunity to show the chemistry that is all around us. Choosing food items makes the experiment nontoxic, biodegradable, and environmentally friendly. In addition, it is also cost-effective both when it comes to purchase and waste handling. The average cost for a 1 cm thick hydrogel made with commercial chemicals in a 90 mm Petri dish, including the copper wire, is 0.28 euros. The Petri dish is not included in the price, nor is the battery. Most importantly, this makes the experiment accessible not only for teachers without a laboratory (e.g., in elementary school) but also for students who want to continue the experiment at home. We have chosen to use magnesium sulfate for the same reasons as we have chosen the other components. It is inexpensive, nontoxic, biodegradable, easily obtainable, and easy to handle, even though sodium sulfate is more commonly used for the electrolysis of water especially when pH determination is also important.[8] The magnesium ion (Mg^{2+}) also enhances the gelation of the carrageenan compared to the sodium ion (Na^{+}).[12] An increasing concentration of Mg^{2+} will, however, decrease the hardness of the hydrogel.[19] Other gel-based electrolysis setups have been seen in this *Journal* earlier, using gelatin-based gels, both for illustrating color changes and for making microscale setups.[6,8] Our hydrogel can be utilized also for these kinds of experiments and works well for a color changing reaction as it is highly transparent in its native form (i.e., without indicators present).

The visiting groups are usually very diverse, regarding both interest in and knowledge of chemistry. Some are very interested and have solid knowledge; others lack interest and have difficulties even with very basic concepts. This means that some students need more help than others; we have still decided not to give too many recipe-like instructions. Instead, we have made sure to have enough instructors present to enable discussion for those who need help. This also gives the instructor the opportunity to meet the students at their level. Suggestions for strategies on how to help the more unprepared students can be found in the second Lab Work heading (Lab Work for Classroom−Writing Board) in the Student Notes portion of the Supporting Information, as this work has been developed on the basis of our discussions with the visiting students. The laboratory time for our visiting groups varies between 30 and 60 min, with 30 min being the more common option. Due to the short time, we usually have very little time for further discussions. However, with more time on one’s hands or if someone is using this in a classroom setting, we see this as a great opportunity to take the demonstration further by discussing topics like green chemistry and the need for reducing waste, especially hazardous waste. The Petri dish used in the experiment, whether it is plastic or glass, can and should be cleaned and reused in other experiments. Plastic as a material has gained a lot of negative publicity in recent times and can be exchanged for something more recyclable like a drink carton. The battery can be exchanged for a small hand driven motor or solar cell.

We have used this experiment as an outreach activity for upper secondary students. However, it is possible to use it also with younger students as a more structured activity with more specific instructions. In this case, we recommend to at least start with using the cathode (the negative terminal of the battery) for writing as this reaction gives a much quicker response. The instructions for the outreach activity are based on limited time resources. We have noticed that some of the students are struggling with basic concepts, so we have therefore also developed instructions for classroom settings based on our experiences with the visiting students. These can be found in the Supporting Information.

The positive outcomes of combining science and art, as well as the benefits of using everyday items, have been addressed by several authors.[2,20,21] Our overall impression is that, also, the students we have encountered really enjoyed both the artistic elements and the freedom of creativity of the experiment very much.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available at https://pubs.acs.org/doi/10.1021/acs.jchemed.0c00440.

> Notes for instructors, including more detailed instructions on how to prepare the gel; additional photographs of the gel and the setups; and student notes for two versions of the writing board experiment (PDF, DOCX)

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Notes

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(Calcium-Phosphate)/Carrageenan Gardens Grown from the Gel/Liquid Interface

Anna Fogde, Syeda Qudsia, Trung-Anh Le, Thomas Sandberg, and Tan-Phat Huynh*[a]

In this study, a gel/liquid interface is utilized for growing a new (calcium-phosphate)/carrageenan garden. The hydrogels are made from carrageenan loaded with either sodium phosphate or calcium chloride, while the interfaced solution contains a source of the salt not used in the hydrogels (i.e. the sodium-phosphate hydrogel with the calcium-chloride solution and vice versa). The physical and chemical properties of tubes grown from both systems of the same amount of carrageenan have been reported. Interestingly, when varying the amounts of carrageenan (and thus controlling the stiffness of the phosphate-hydrogel system), it is possible to control the thickness and height of the tubes.

1. Introduction

Self-organizing precipitation processes such as chemical gardens (or chemobrionics) forming typical micro- and nano-tubular forms, have the potential to drastically influence the design of future materials which contribute to a wide range of applications including fuel cells, chemical sensors, and drug delivery.[1] Additionally, the processes allow us to develop new methodologies to explore, quantify and understand non-equilibrium chemical systems, and might even shed light on conditions for the origin of life.[1a,c,2] Traditional chemical gardens are grown from a system when a salt seed is placed in a counterion solution. More interesting morphologies as well as physical and chemical properties have been found when gardens evolve from a gel/liquid interface.[3] As the gel (or hydrogel) part plays the role of the seed, it should be formulated in a suitable condition depending on the initial selection of polymers. For example, chemical gardens of calcium phosphates – the potentially artificial bone-like material, are grown from the gel/liquid interface of which the hydrogels are made of water-soluble biopolymers such as gelatin[4] and agar.[5] We however believe that more hydrogel systems can be exploited to create calcium-phosphate gardens.

In our recent work, κ-carrageenan is complexed with Mg^{2+} to form hydrogels which have interesting features to be used as colorimetric and electrolytic materials.[6] Carrageenans are a family of linear sulfated polysaccharides that can be extracted from some species of red algae (*Rhodophyta*). Even though there are up to 15 different structure types of carrageenans, the ones that are found most in red algae are κ-, ι- and λ-carrageenan with the difference between them being the number and position of sulfate groups.[7] Structure-wise, carrageenans are hydrophilic linear sulfated galactans, consisting mainly of alternating 3-linked β-D-galactopyranose (G-units) and 4-linked α-D-galactopyranose (D-units) or 4-linked 3,6-anhydro-α-D-galactopyranose (DA-units) that are forming the repeating disaccharide unit in the structure.[8] Owning to physical functional properties such as the ability of thickening, gelling, stabilizing, carrageenans are used in places like food, cosmetic and pharmaceutical industries. In material design, some mineralized composites of calcium phosphates and carrageenan prepared using gel/liquid approach have been reported,[7,9] but, to the best of our knowledge, no calcium-phosphate gardens grown from carrageenan-based hydrogel have been observed. This work therefore reports the suitable conditions for growing tubular structures of calcium phosphate from the interface of carrageenan-salted hydrogels, particularly the (calcium chloride)-based hydrogel (*Ca-gel*) or (sodium phosphate)-based hydrogel (*P-gel*), and solutions of counter ions. For the sake of convenience, *Ca-gel* and *P-gel* are used to name the systems (also including the upper liquid) of which the tubes were grown. Additionally, the study has revealed how the stiffness of the hydrogel influences the growth of P-gel tubular structures.

Experiment

Materials

Calcium chloride dihydrate, trisodium phosphate (tert) dodecahydrate, sodium hydroxide, hydrochloric acid 37% (analytical grade) were obtained from Merck. Food-grade kappa-carrageenan powder from Specialingredient was purchased through Amazon. Ethanol (99.5%) was obtained from Altia, Finland and was used together with distilled water for washing.

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An invited contribution to a Special Collection on Chemobrionics

Preparation of Hydrogels

Hydrogels were prepared by mixing carrageenan into room temperature solutions of tri-sodium phosphate or calcium chloride and pH of the solutions was adjusted using hydrochloric acid and/or sodium hydroxide. The mixtures were stirred while heating for 30 minutes using a heating plate with magnetic stirrer. The temperature of the heating plate was kept as a constant, therefore the heat of the solutions varied between 75–85 °C. The solutions were transferred into beakers and left standing at room temperature for cooling down and setting. Depending on the wt% of carrageenan, the cooling down and setting of the hydrogel took place for 15–35 minutes before the next step (see 2.3). The different compositions of hydrogels that were made can be found in Table 1.

Growth of Tubular Structures

The tubular structures were grown from the gel/liquid interface by adding a solution of 0.1 M calcium dichloride, while the tubular structures based on a calcium hydrogel were grown from the gel/liquid interface by adding a solution of 0.05 M trisodium phosphate, keeping the ratio between solution and hydrogel equal to 5:2 (v:v). The beakers containing the growing systems are placed on a stable table without disturbance during the growth process.

While the focus of the study was the hardness of the hydrogel (Table 1), some additional tests were done to investigate the possibility to enhance or diversify the growth (Table S1). These included heating the $CaCl_2$ solution (45 °C), adding a NaCl hydrogel layer, lowering the carrageenan amount below 1 wt%, increasing the concentration (0.3 M, 0.5 M) or lowering the pH of the Na_3PO_4 solution used for the hydrogel and lowering the concentration (0.05 M) or making changes to the pH (2.5, 3.5, 6) of the $CaCl_2$ solution. All except for the changes in the pH of the $CaCl_2$ solution were unsuccessful, but none of the tests showed any increase in the growth.

Characterization of Tubular Structures

Before characterization, the tubes were purified to remove any excess solution or extra material (e.g., non-tubular reactions in the gel-solution interface). The tubes were transferred from the beaker using a plastic pipette and washed twice with distilled water and twice with ethanol (99.5 %).

Pictures during the growth process were taken with a mobile phone camera approximately 3 h after the solution had been added. Pictures of the different tubes were also taken using the Olympus SZX12 stereo microscope with a Nikon Coolpix camera. LEO Gemini 1530 scanning electron microscope with thermo scientific ultradry silicon drift detector was used to study the morphology of different samples. The instrument is equipped with a Thermo Scientific UltraDry SDD EDS-system which makes it possible to do elemental analysis on samples. The collected tubes were placed on a glass substrate and sputtered with Pt.

X-ray diffraction (XRD) pattern of the grown tubular structures were obtained with a Bruker D8 Discover instrument by using a scintillation detector and copper Kα radiation ($\lambda = 1.54$ Å). The measurements were performed using powder XRD mode in the 2 theta range 5° to 80°, using a step size of 0.04°. The obtained diffractograms were analyzed by matching against patterns from the ICDD database using Eva software from Bruker. For the XRD samples, tubes of all sizes were extracted from the solution after 1–3 days, and the Ca-gel tubes were extracted before they could reach the surface of the solution (within an hour).

Netzch STA 449 F1 Jupiter thermogravimetric analyzer was employed under N_2 inert atmosphere from 30 to 600 °C at a heating rate of 10 °C min^{-1}. N_2 flow rate was kept at 20 mL min^{-1}. Dry samples were kept in vacuum before the measurements and 2–10 mg of the dry samples were transferred to aluminium thermogravimetric Analysis (TGA) pans. Derivative thermogravimetric (DTG) curves were plotted to detect significant weight changes of all samples.

Table 1. Conditions for syntheses of the tubular structures when the Ca-gel or P-gel system was used.

Hydrogel	Solution	$V_{Na3PO4}:V_{CaCl2}$	Carrageenan in the hydrogel [wt%]	Setting time of hydrogel [min]
Ca gel				
0.1 M $CaCl_2$ pH 4.5	0.05 M Na_3PO_4 pH 12.9	5:2	1.5	30
P gel				
0.1 M Na_3PO_4 pH 12.9	0.1 M $CaCl_2$ pH 4.5	2:5	1.0	35
0.1 M Na_3PO_4 pH 12.9	0.1 M $CaCl_2$ pH 4.5	2:5	1.5	20
0.1 M Na_3PO_4 pH 12.9	0.1 M $CaCl_2$ pH 4.5	2:5	2.0	15
0.1 M Na_3PO_4 pH 12.9	0.1 M $CaCl_2$ pH 4.5	2:5	3.0	15
0.1 M Na_3PO_4 pH 12.9	0.1 M $CaCl_2$ pH 4.5	2:5	4.0	15

2. Results and Discussion

In this study, the syntheses and characterizations have been focused on tubes which were grown from the calcium- and phosphate-based hydrogels consisted of 1.5 wt% of carrageenan. As we have shown in our earlier study[6] that it gives an excellent hydrogel with Epsom salt (Mg^{2+}), this was our first choice regarding the amount of carrageenan to begin with. Therefore, the ions of interest (Ca^{2+} and PO_4^{3-}) have been tested under mentioned condition.

While the concentration of salts in both P-gels and Ca-gels were 0.1 M, the corresponding solutions (for the best growth) had different concentrations of calcium or phosphate ions (Table 1). Hughes et al.[5a] reported a considerable growth of tubes with a concentration ratio of 1:1 ($Ca^{2+}:PO_4^{3-}$) whereas Ibsen et al.[4] reported maximum yield of tubes with concentration of the ion in solution being half of that of the ion in the hydrogel. This variation is possibly caused by the selection of biopolymer, i.e. agar[5a] and gelatin[4] for the former and latter works, respectively. In our study, the hydrogel phase of the system is based on carrageenan. The tubes grew progressively from the Ca-gel system when the concentration of the PO_4^{3-} was half of that of Ca^{2+} in the hydrogel (0.05 M) (Figure S1B), but only grew in limited fashion along the walls of the beaker when the concentration was the same (0.1 M) (Figure S1A). Conversely, tubes grew from the P-gel system when the Ca^{2+} concentration in the solution was the same (0.1 M) but not when it was halved (0.05 M). We assume that this is due to the nature of the sulfate group of κ-carrageenan, as cations enhance the hydrogel formation and Ca^{2+} does more so than

Na^+.[8b] In order for the tubes to grow from the interface, there needs to be a mineralized layer established at the interface that works as a barrier, allowing for a buildup of osmotic pressure. When the osmotic pressure is high enough, the membrane ruptures and the ions (Ca^{2+} or PO_4^{3-}) together with carrageenan molecules shoot into the liquid phase resulting in tubular structures. Thus, in the absence of a suitable (neither too thin nor too thick) barrier/membrane formed by the concentration shown in Table 1, no growth can take place. This influence has been partly reported in the work of Ibsen et al.[4] As the Ca^{2+} ions play a role as crosslinkers (whereas PO_4^{3-} does not) of the hydrogel matrix, the use of Ca^{2+} ions for the growth of the tubes will affect the available amount of Ca^{2+}. In Ca-gel system, when the concentration of Ca^{2+} (in the gel) and PO_4^{3-} (in the solution) are equal to 0.1 M, the mineralized membrane becomes too thick (due to high PO_4^{3-} concentration), making fractures rare and therefore limits driving forces for Ca^{2+} shooting across the interface. If the concentration of PO_4^{3-} (in the solution) is halved, a suitable-thickness membrane forms which the tubes can grow. In P-gel system, when the concentration Ca^{2+} (in the solution) is the same as that of the PO_4^{3-} (in the gel), the formed membrane is sufficiently thick to result in the growth of the tubes. However, if the concentration of Ca^{2+} (in the solution) is lowered to half of that, no build-up of osmotic pressure takes place and thus tubular structures cannot be formed. As the Ca^{2+} ions interact with the hydrogel matrix, they (in the hydrogel or in the solution) will also play a part in the macrostructure of the tubes. When the Ca^{2+} ions are in solution, they will partly diffuse into the gel making the top layer of the hydrogel stiffer. This process will slow down the diffusion of PO_4^{3-}, making the tubes much smaller in height than the tubes grown from the Ca-gel, as can be seen in Figure 1A, B.

2.1. Morphology of Tubular Structures

Figure 1 shows that the tubes of one particular hydrogel are not necessarily the same in form and thickness. To highlight the difference between the Ca-gel and P-gel systems, tubes of the same growth condition regarding the hydrogel, i.e. 1.5 wt% carrageenan, are chosen (Figure 1). The structures from the Ca-gel system grow progressively to the surface (Figure 1A) and continue to grow along the surface as is illustrated by Figure S1A&B in the Supporting information. If the tubes are grown in a cylinder (Figure S1C), we have managed to grow tubes as tall as 12–13 cm before they fall against the walls of the cylinder but continue growing in a more winding path. As the growth of Ca-gel tubes causes a coating to form on the surface of the liquid, the tubes must be extracted for characterizations before this coating has developed. Once the tubes have been removed, new ones will grow thereafter. This phenomenon is most obvious in the Ca-gel system.

On the other hand, all tubular structures based on the P-gel systems (Figure 1e and S2) have limited growth in height and remain fully within the liquid. This can be seen by optical microscope and SEM pictures (Figure 1). For comparison, the larger tubes from the Ca-gel (Figures 1B–D) and from the P-gel (Figures 1F–H) systems of 1.5 wt% carrageenan are shown. Clear difference in the alignment of the tubes can be seen in microscopic images (Figures 1B and 1F), i.e. the tubular structures from the Ca-gel system are all straight while those from the P-gel system are curved. Both types of tubes show three different domains at the cross-section of the tubes including the ball structure on the outside, a thick wall, and a brick-like inner structure. In addition, the grown Ca-gel and P-gel tubes are different in diameter which can be seen in the SEM images of Figure 1C–D and 1G–H. At the first glance, the P-gel is more porous than the Ca-gel. However, the mid layer of the P-gel tube (~2 um) is much thicker compared to that of the Ca-gel (< 0.5 um). Additionally, it is possible to distinguish a difference in the precipitate on the outer tube walls.

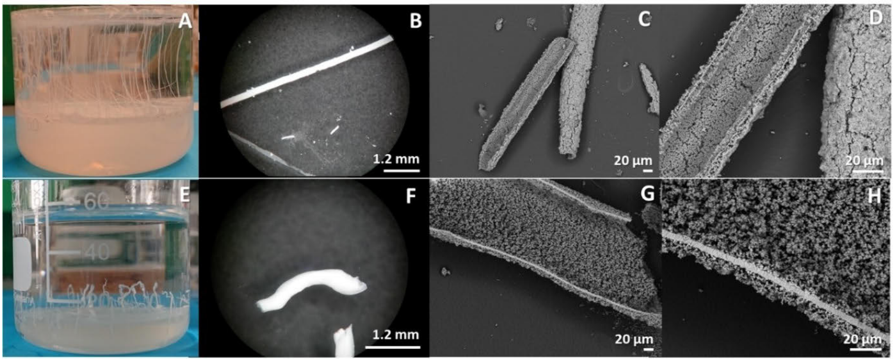

Figure 1. Microscopic investigation of the tubular structures grown from Ca-gel and phosphate liquid (A–D); and P-gel and calcium liquid (E–H) interfaces. Images are taken with a camera (A, E), optical microscope (B, F), and SEM (C, D, G, H).

As the P-gel system exhibits limited growth of the tubes, it is a preferable model to study the effect of hydrogel stiffness on the growth. Depending on the amount of carrageenan used for each hydrogel, a clear colour difference in the hydrogels is observed (Figure S2). This is due to the difference in viscosity, leading to the thicker hydrogels reaching a higher temperature. Besides, the height and thickness of the tubes decreases with increasing amount of carrageenan. The porosity of the P-gel tube decreases when higher wt% carrageenan is used, and an especially closer look is taken on the walls of tubes grown from P-gel systems with 1 wt% carrageenan and 1.5 wt% carrageenan (Figure S4&S5). In both cases it is possible to distinguish differences between the structures on the inner walls (inside the tube) and the outer walls. It is also possible to distinguish between these structures among the tubes made from different gels.

2.2. Chemical Analysis of the Tubular Structures

Not only is the tube's morphology different, but their chemical structures also are distinctly different which are revealed by energy dispersive X-ray spectroscopy (EDX). Element mapping showed relatively similar chemical composition for both P-gel and Ca-gel tubes at the regions 1, 2, and 3 where the main elements are Ca, P, and O (Figure 2). Table S2 summarizes the

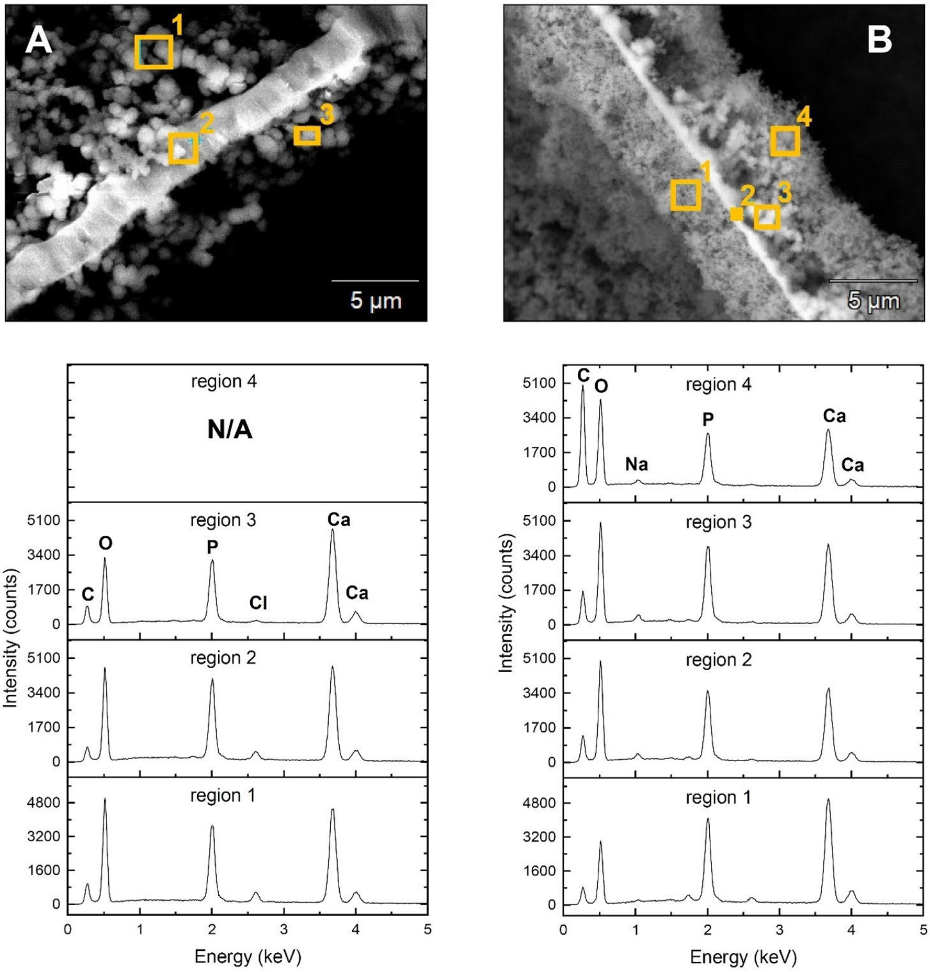

Figure 2. Cross-section of the tubes and EDX spectra at different regions of the walls of the tube grown from P-gel (A) and Ca-gel systems (B).

atom percentage (%) of four main elements (Ca, P, O, and C) at different regions of the walls of the tube, calculated from the EDX spectra of Figure 2. This is an indirect proof that both tubes are formed by calcium phosphate. But different from P-gel tube, the Ca-gel one possesses an extra layer, that can be seen in region 4 in Figure 2B, where an intensive signal of C is found, indicating the presence of carrageenan. Interestingly, there is no signal of Na found in the P-gel but found at all region of the Ca-gel tube, while the signal of Cl appeared in P-gel but not in the Ca-gel tube. These two signals are believed to be from the liquid fractions, i.e. Na (Na_3PO_4) and Cl ($CaCl_2$) for the Ca-gel and P-gel systems, respectively.

To further investigate the difference between the Ca-gel and the P-gel systems, tubes were characterized using XRD. Figure S6 shows the X-ray diffraction patterns of both kinds of tubes, also including a pattern for the sample holder. Due to the small amounts of the collected samples, a stronger background signal can be seen from our sample holder (broad peak at around 12 degrees). However, Figure S6 can still expose the diffraction patterns of the two different kinds of tubes. The Ca-gel sample is amorphous and shows no signs of being crystalline. This is also validated by the fact that after evaporation of the washing ethanol, the tubes have lost their form and turned to powder, which does not occur for the P-gel tubes. The diffraction pattern shows two broad peaks, one at 12 degrees and one at 30 degrees, both are likely due to the background from the sample holder. A contributing factor for the lack of crystalline material in the Ca-gel tubes could be the very short amount of time the tubes are in the solution. For example, Hughes *et al.*[5a] and Kim *et al.*[10] report changes in the diffraction patterns with time. The diffraction pattern for the tubes from the P-gel system can be seen in Figure S6. This pattern includes the broad peak at 12 degrees from the background. The shape of the non-flat baseline could be from the background or due to a partly amorphous sample. When comparing the graphs against known patterns, we have looked at the peaks at approximately 26, 28, 32, 39.5, 44, 47, 49.5, 53, 62, 64.5 and 75 degrees, which match closely against calcium hydroxylapatite ($Ca_9HPO_4(PO_4)_5OH$) (JCPDS #00-046-0905).[11] The difference in crystallinity might also be explained by the differences in pH of the solutions in which the tubular growth takes place. A higher pH is likely to give a more amorphous material.[12] In addition, not only are the Ca-gel tubes in solution for a much shorter period but the growth itself is also very rapid in comparison to that of the P-gel tubes. We expect that both pH and time in solution[13] play a part of the resulting difference in the crystallinity.

Figure S7 illustrates the TGA and DTG curves of the two samples. Below 200 °C, all the samples exhibit gradual weight losses due to the removal of adsorbed and lattice water. Amorphous Ca-gel tubes have a greater water weight loss of 10.16% comparing to crystalline P-gel tubes with a water weight loss of 8.10%. This is consistent to the phase structures of the two materials since crystallization reduces the adsorbed water content and/or it is more difficult to remove lattice water in crystalline structures. Thermal degradation of remaining κ-carrageenan is observed at around 250–286 °C in both samples. This corresponds to small weight losses of 6.29 and 1.83% in Ca-gel and P-gel tubes respectively.[14] As the temperature increases up to 600 °C, subsequent thermal degradation of κ-carrageenan continues while calcium phosphate remains thermally stable. Phase transformation of amorphous calcium phosphate into b-tricalcium phosphate and a-tricalcium phosphate might occur starting from 530 °C approximately.[11]

3. Conclusions

In this work we have utilized hydrogels to grow tubular calcium-phosphate structures from a gel/liquid interface. The Ca-gel system achieves excellent growth in the numbers of tubes which are straight and long but amorphous, whereas the P-gel one gives fewer, shorter, and more curved tubes of which the calcium-hydroxylapatite crystallinity is found. Moreover, by controlling the stiffness of the hydrogel (the amount of κ-carrageenan added) of the P-gel system we can control the height and especially the thickness of the tubes. It is worth mentioning that we have chosen to use commercial carrageenan (bought through Amazon) as it is readily available for anyone at fair price, and especially have proven it possible to grow tubular structures using such commercial material. Therefore, we consider this work to also open new doors in the use of chemical gardens in both research and education settings.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: calcium phosphate · carrageenan · chemical gardens · interfaces · tubular structures

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III

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SUPPORTING MATERIAL

THE TABLE and THE TUBES

Photo: Jan-Erik Andersson

Pöytä ja putket

KUVATAITEILIJA JAN-ERIK ANDERSSON JA TUTKIJA TAN PHAT HUYNH, AVUSTAJANA TUTKIJA ANNA FOGDE

Tämä työ on osa poikkitieteellistä, tutkijatohtori Laura Hellstenin johtamaa *Avtryck i det Okända – Jälki tuntemattomaan* – projektia, jossa tiede ja taide tekevät yhteisen matkan tieteellisen kommunikaation äärelle. Projekti saattaa Åbo Akademin huippututkijat saman pöydän ääreen taiteilijoiden kanssa. Näin tutkijat saavat harjoitella tutkimuksensa esittelyä tiedeyhteisön ulkopuolella ja taiteilijat tulkitsevat ja kuvittavat näkemäänsä, kuulemaansa ja tuntemaansa valitsemallaan tavalla. Tutkijat ja artistit ovat omien ryhmiensä kesken valinneet, onko valmis työ tasapuolinen ponnistus niin tieteen kuin taiteen osalta vai esiintyvätkö eri osa-alueet rinnakkain teoksessa.

Tämä vihkonen, jota juuri luet, on tutkijoiden ja taiteilijoiden yhteinen keskustelunavaus yleisön kanssa - sinun kanssasi. Pöytä ja putket –projekti sisältää vihkosen lisäksi teoksen, joka koostuu kuvataiteilija Jan-Erik Anderssonin luomasta pöytäveistoksesta sekä pöydän päällä olevaan maljakkoon kasvatetusta kemiallisesta puutarhasta, jonka ovat toteuttaneet tohtori Tan Phat Huynh ja väitöskirjatutkija Anna Fogde.

Jan-Erik: Minulle keskeistä elämän tarkoituksessa on aina ollut kysymys siitä, mitä ”elossa” oleminen tarkoittaa. Ollessani nuori 1960-luvulla kouluopetus ei koskaan tuntunut painottavan sitä, kuinka monet käsitteet ja rajat ovat hyvin häilyviä ja että terävien, kiistämättömien totuuksien sijaan maailma on kuin loputtomien muunnosten kirjo. Ainakin lähempää tarkastellessa huomaa, että luonto synnyttää uusia muunnoksia jatkuvasti.

Nyt kun tekoäly on kyseenalaistanut ”ihmismielen” ainutlaatuisuuden, myös elämän alkuperä sekä elävän ja elottoman välinen raja on epäselvä. Tutkijat puhuvat ”epäorgaanisesta biologiasta” yrittäessään valmistaa itsekopioituvia ja -kehittyviä soluja, jotka kykenevät jopa varastoimaan sähköä - aivan kuten orgaaniset, biologiset solut.[1] Albert Szent-Gyorgin sanoin: ”Elämä ei ole muuta kuin elektroni etsimässä lepopaikkaa.”

Oli kiehtovaa tarkastella Kemiallista puutarhaa ensimmäisen kerran Phatin ja Annan kanssa ja huomata epäorgaanisten, kasvavien rakenteiden kauneus. Niin ylivoimaisen kauniina pidetty eloperäinen luonto, kuin myös epäorgaaniset rakenteetkin, pitävät sisällään paljon kauneutta.

Phat & Anna: Mitä ovat nämä Kemialliset puutarhat? Kirjaimellisestihan ne ovat "saostuneiden kemiallisten olomuotojen puutarhoja". Kemiallinen puutarha on kemiallisten reaktioiden sekä fyysisten prosessien tuote, joka synnyttää ylöspäin kasvavan rakenteen ja kasvimaisia piirteitä. Tavallisesti niihin käytetään kauniinvärisiä metallisuoloja ja tämän vuoksi ne ovat erittäin suosittuja luonnontieteen luokkahuoneissa. Ja miksi sitten puhumme putkista? Koska putkimainen rakenne on kemiallisten puutarhojen peruspiirre. Puutarhan kasvuprosessi tekee rakenteista onttoja ja siksi ne voidaan nähdä ikään kuin putkina (kuva sivu 30).

Puhumme näistä rakenteista ikään kuin kasvavina. Pidämmekö niitä siis elävinä? Milloin ylipäätään voi jonkin käsittää elävän, eläväksi? Kemialliset puutarhat ja elämän alkuperä jakavat yhteisiä piirteitä tavassa, miten kalvorakenne muodostuu. Jatkakaamme siis kiehtovaa matkaamme kysymyksemme parissa tarkastelemalla Stéphane Leducin kemiallisista puutarhoista kertovaa lainausta kirjasta "Elämän mekanismi":

"Osmoottisen kasvun ilmiöt osoittavat kuinka tavanomaiset mineraalit, karbonaatit, fosfaatit, silikaatit, nitraatit ja kloridit, saattavat imitoida elollista luontoa ilman yhdenkään elävän organismin väliintuloa. Tavalliset fysiikan voimat kykenevät yksinään tuottamaan elävien olentojen kaltaisia muotoja, osmoottisten kalvojen kautta erottuneiden nesteiden täyttämiä onkaloita, ja sisäelinten kudosta muodollaan, värillään, kehityksellään ja toiminnallaan muistuttavia rakenteita… Näiden pitkien aikojen saatossa on muinaisissa vesissä saattanut olla runsain määrin osmoottista kasvua. Kaikki aineet, jotka kykenivät muodostamaan yhdessä osmoottisia kalvoja, alkoivat kasvaa runsain mitoin: kalsiumin, karbonaattien, fosfaattien, silikaattien ja albumiinien liukoiset suolat järjestäytyivät osmoottisiksi tuotoiksi, syntyivät, kehittyivät, hajosivat ja kuolivat. Miljoonat lyhytikäiset muodot ovat varmasti seuranneet toisiaan luonnollisessa evoluutiossa sinä aikana, jolloin elävää maailmaa edustivat osmoosin avulla järjestäytyneet aineet."[2]

Kysymys siitä, mitä elämä on ja mitä elossa oleminen tarkoittaa, kiehtoo monia ihmisiä niin tieteen piirissä kuin sen ulkopuolellakin. Toinen kiinnostava kysymys on elämän alkuperä, mistä elämä oikein alkoi? Tieteessä elämän alkuperää kuvataan usein edelleen osin tuntemattomilla prosesseilla, jotka alkoivat muuttaa elotonta ainetta elolliseksi. On kuitenkin tiedossa, että syvällä merenpohjalla sijaitsevissa kuumissa lähteissä elää kaikkein vanhimpia tunnettuja elämänmuotoja. Kuumien lähteiden ympäristössä on saatavilla kaikki tärkeimmät prebioottiset molekyylit (vety, metaani, ammoniakki, hiilidioksidi ja nitraatit) joita tarvitaan biosynteesin syntyyn. Onkin mielenkiintoista, kuinka voimme löytää näitä samoja prosesseja kemiallisista puutarhoista, erilaisina virtauksina *läpi kalvojen, jotka hallitsevat esimerkiksi elektronien ja protonien virtauksia. Sen lisäksi tieteilijät ovat kyenneet havainnollistamaan reaktioita, jotka* saattavat mahdollistaa jopa autotrofisen* aineenvaihdunnan.[3] *Jäljelle jää kuitenkin vielä useita* vastaamattomia kysymyksiä siitä, kuinka elämä kehittyi prebioottisista molekyyleistä. Etsiessämme vastauksia näihin kysymyksiin meidän tulisi tutkia huolellisesti kemiallisten puutarhojen kalvojen lävitse kulkevia virtauksia.

Haluaisimme kutsua yleisön mukaan tämän kiehtovan aiheen äärelle tarjoamalla teille mahdollisuuden tarkkailla näitä kalsiumfosfaateista tehtyä putkia (tai toisin sanoen, kemiallista puutarhaa), jotka kasvavat maljakossa pöydän keskellä. Aivan kuten takapihalla kasvava nurmikkokin, nämä putket tarvitsevat kasvaakseen suotuisan ympäristön sekä ravinteita. Tässä tapauksessa ”maaperä” koostuu biopolymeeripohjaisesta geelistä, jossa on ”ravinteina” natriumfosfaattia. Tämä geeli pysyy maljakon pohjalla, kun taas veteen liuennut natriumfosfaatti on maljakon yläosassa. Putkien halkaisijat voivat vaihdella noin 30–40 mikrometrin välillä (saman paksuinen kuin ihmisen hius) ja niitä voidaan tarkastella valomikroskoopin alla.

*autotrofi: eliö, joka kykenee tuottamaan oman ravintonsa yksinkertaisten kemiallisen yhdisteiden, kuten hiilidioksidin, avulla.

Jan-Erik: Mietin paljon tälle haasteelle sopivaa lähestymistapaa. En halunnut tehdä kuvitusmainen teos Kemiallisista puutarhoista. Yhtä lailla oli vaikeaa tehdä edes jonkinlaista tulkintaa Kemiallisista puutarhoista sen perustana olevan kemian vaikean ja käsitteellisen luonteen vuoksi. Siispä päätin luoda *esityksen* Puutarhoista, tai tässä tapauksessa yhden puutarhan. Tavoitteenani oli korostaa puutarhan kauneutta jollakin tapaa ja asettaa se jalustalle, pöydälle, joka myös luo paikan ajatustenvaihdolle.


The Table and the Tubes

Photo: Pekko Vasantola

Olen ollut pitkään kiinnostunut pöydästä käsitteenä *kommunikaation näkökulmasta.* Yleensä, ainakin ennen koronaa, suurin osa kommunikaatiosta tapahtui pöydän ääressä, sen päällä, ja jopa sen alla! Mikäpä siis olisikaan parempi korostamaan Laura Hellstenin tutkimuksen teemaa! Ajattelin myös, että olisi hienoa, jos ihmiset löytäisivät projektimme äärelle sattumalta, mikäli pöytä olisi esillä tavallisessa kahvilassa ja olisi siellä käytössä.

Pöydän keskellä lieriömäisessä lasiastiassa olisi siis Kemiallinen puutarha. Ei mitään monimutkaista filosofiaa tai yritystä ”selittää” monimutkaista kemiallista prosessia visuaalisesti, vaan epäorgaanisen kasvun kauneutta kunniapaikalla.

Alun perin halusin valmistaa koko pöydän epäorgaanisista materiaaleista, mutta myöhemmin päätin tehdä pöydän pinnan betonista, maa-aineesta ja teräksestä ja sille jalat kuudella eri vihreän sävyllä maalatusta kierrätyspuusta.

Jaoin pöydän pinnan kolmeen osaan (ilman sen tarkempaa syytä). Tein sitten muotin betonille, jonka asetin maata vasten saadakseni hieman maa-ainesta pöydän pintaan. Näiden betoniosien väliin asetin rautalevyt, jotka ruostuvat, mikäli ne saavat vettä päälleen.

Karkea betoni voi olla vaativa pinta kahvilan asiakkaalle, joka etsii turvallista (tasaista!) laskualustaa kupilleen. Se on eräänlainen symboli sille epävarmuudelle, jota tunnemme planeettamme orgaanisen elämän puolesta tällä hetkellä.

Anna: Kemialliset reaktiot ja visuaaliset prosessit ovat aina kiehtoneet minua. Ja opettajana, joka on kovin kiinnostunut tieteellisestä kommunikaatiosta, on tämä mahdollisuus laajentaa tieteellisetä näköpiiriäni ja rakkauttani tiedettä kohtaan ollut ihmeellinen seikkailu. On ollut kunnia osallistua tähän ajatusprosessiin, jonka kemiallinen työmme on herättänyt muissa ihmisissä ja on ollut erittäin kiinnostavaa seurata Jan-Erikin työtä meidän kemiallisten puutarhojemmeympärillä.

Jan-Erik: Juttelin projektistamme erään ihmisen kanssa ja koetin selittää orgaanisen ja epäorgaanisen välistä eroa kertomalla, että orgaaninen kemia koskee hiiliperäisten yhdisteitä ja epäorgaaninen puolestaan kaikkia ”kuolleita” asioita. Hän tuohtui kovasti ja sanoi, että kaikki kivet ovat ”eläviä”. Mietin, kuinka vanhentuneita minun käsitykseni kemiasta ja elämästä ovat tällä posthumanistisella aikakaudella, jolloin ihmiset eivät enää olekaan tärkein laji planeetallamme.

Jan-Erik, Phat ja Anna: Kutsumme nyt sinut, lukija ja tarkkailija, jakamaan ajatuksesi projektistamme. Jaa ne meidän kanssamme, ystäviesi kanssa tai vain hiljaisina ajatuksina maailmankaikkeuden kanssa. Me toivomme, että sinulla on mahdollisuus nauttia hetken aikaa maailman kauneudesta projektimme parissa.

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Photo: Robert Seger

OLEN JAN-ERIK ANDERSSON, laaja-alaisesti installaatioiden, veistosten, mediatöiden, ympäristöteosten sekä arkkitehtuurin parissa työskentelevä kuvataiteilija. Olen syntyperäinen turkulainen, ja Turku on yhä maailmankaikkeuteni keskipiste; asun Hirvensalon saarella Lehtitalossa (Life on a Leaf), joka on kokonaisvaltainen taideteos ja myös minun väitöstyöni Helsingin Kuvataideakatemialle.

Olen erittäin kiinnostunut siitä, kuinka elämä ja tutkimus voidaan yhdistää taiteelliseen työhöni. Olen onnekas saadessani nauttia valtion taiteilijaneläkkeestä, joka antaa minulle vapauden tutkia mitä ikinä haluan! Tällä hetkellä suunnittelen kuusikulmaista hirsitaloa taiteellisilla erityispiirteillä.

Minulla on luonnontieteellinen tausta Åbo Akademilta, jossa opiskelin orgaanista kemiaa, biologiaa, kasvitiedettä ja taidehistoriaa. Olen myös valmistunut Turun Taideakatemiasta ja minulla on kuvataiteen tohtoritutkinto Helsingin Kuvataideakatemiasta, jossa toimin tutkijatohtorina tällä hetkellä. Pääasiallinen kiinnostuksen kohteeni on, kuinka taide voi luoda arkkitehtuurisia tiloja sekä yhteistyöprosessit taiteilijoiden ja arkkitehtien välillä.

NIMENI ON ANNA FOGDE ja olen iloinen sekä utelias tohtoriopiskelija fysikaalisen kemian alalla. Olen kotoisin Maarianhaminasta Ahvenanmaalla, mutta olen asunut Turussa opintojeni alusta asti. Mielestäni maailma on pullollaan fantastisia ja jännittäviä ilmiöitä, ja vaikka ensimmäiset kouluvuoteni ovat jo kaukana takanapäin, olen yhä lapsenomaisen innoissani kaalimehuista, saippuakuplista sekä nappuloiden painelusta.

Tutkimustyössäni olen erityisen kiinnostunut siitä, mitä tapahtuu pinnoilla sekä rajapinnoilla. Tällä hetkellä tutkin geelien ja nesteiden rajapinnoilla muodostuvien aineiden ominaisuuksia. Teen yhteistyötä Tan Phat Huynhin kanssa. Niin kuin hän tapaa huomauttaa esityksissään, materiaalimme eivät ole vain ominaisuuksiltaan kiinnostavia, vaan myös kauniita katsella. Olen myös kiinnostunut kokeilemaan, kuinka yksinkertaisten materiaalien kanssa voi työskennellä (kuitenkaan tuloksia uhraamatta). Sen lisäksi että olen kemisti, olen myös aineopettaja ja etsin aina uusia esittelytapoja tutkimustyölleni erilaisiin opetusympäristöihin. Minun silmissäni yksinkertaiset keinot ja menetelmät ovat tapa tuoda tutkimustyö luokkahuoneisiin ilman suurien kulujen luomaa estettä tai tarvetta luottaa monimutkaisiin laitteisiin.

Olen Tan Phat Huynh ja olen kotoisin Vietnamista. Asun tällä hetkellä Turussa Puolasta kotoisin olevan vaimoni sekä puolitoistavuotisen tyttäreni kanssa.

Tutkimustyöni käsittelee supramolekulaarisia materiaaleja, ja tässä yhteydessä ”supra” tarkoittaa ”korkeampaa”. Nämä supramolekulaariset materiaalit, joita ryhmämme on kehittänyt, ovat niin rakenteeltaan kuin toiminnaltaan edistyksellisiä ja tämän vuoksi lupaavia materiaaleja lääketieteen ja ympäristön tutkimukseen ja ne ovat sen lisäksi myös erittäin kauniita (esimerkiksi Kemialliset puutarhat). Tutkimustyön lisäksi nautin luonnossa liikkumisesta perheeni kanssa. Tykkään myös viettää aikaa ja käydä vaikkapa oluella ystävieni kanssa.

Photos: Jan-Erik Andersson, Pekko Vasantola

Bordet och tuberna

BILDKONSTNÄR JAN-ERIK ANDERSSON MED FORSKAREN TAN PHAT HUYNH, ASSISTERAD AV FORSKAREN ANNA FOGDE

Projektet är en del av *Avtryck i det okända – Forcing the Impossible*, ett mångvetenskapligt- och konstnärligt forskningsprojekt vid Åbo Akademi, som leds av av postdoc forskaren Laura Hellsten. Lauras projekt för samman forskare och konstnärer, där forskare får öva sig i att prata om sin forskning utanför vetenskapsgemenskapen. Konstnärerna illustrerar och tolkar det de hör med hjälp av sina respektive medier.
Inom dessa grupper har man självständigt kunnat bestämma ifall projektet engagerat forskare och konstnärer att jobba ihop på lika grunder, eller om man satsat mera på att utforska den artistiska delen och forskningsdelen, som parallella spår.

Broschyren ni håller i handen gjordes för att utvidga diskussion att också omfatta publiken. Utöver broschyren, omfattar *Bordet och tuberna* ett café-bord tillverkat av bildkonstnär Jan-Erik Andersson och en kemisk trädgård presenterad i en vas, placerad i mitten av bordet, av forskarna Tan Phat Huynh och Anna Fogde.

Jan-Erik: För mig har frågan om vad livet är, vad som är ”levande”, alltid varit av stor betydelse. När jag var ung, under 1960-talet, poängterades det sällan i skolundervisningen hur flytande och vaga många av de begrepp, vilka presenterades som sanningar, egentligen är. I stället för skarpt formulerade sanningar, som inte går att ifrågasätta, är världen i själva verket uppbyggd av flytande spektrum med ändlösa variationer. Åtminstone när man börjar studera omgivningen mera noggrant, märker man att naturen producerar nya variationer hela tiden.

Nu när AI (artificiell intelligens) ifrågasätter det unika med mänskans ”medvetande”, har även livets uppkomst, samt gränsen mellan vad som kan anses vara levande och icke-levande, ifrågasatts. En del forskare talar om ”oorganisk biologi” när de försöker skapa själv-replikerande oorganiska celler som utvecklas och vilka även kan spara elektricitet, precis på samma sätt som organiska, biologiska, kol-baserade celler gör. Eller som Albert Szent-Gyorgi uttrycker det: ”Livet är inget annat än en elektron, som söker efter en plats att vila sig”.

Det har varit fascinerande att för första gången bekanta sig med de kemiska trädgårdar, vilka Phat och Anna producerat och uppleva den visuella skönhet, som dessa oorganiska, växande strukturer innehar. På samma sätt som den organiska naturen ansågs, åtminstone tidigare, besitta en yttersta "skönhet", kan man med goda skäl säga att även de oorganiska strukturerna uttrycker en skönhet.

Phat och Anna: Vad är kemiska trädgårdar? I allmänna ordalag menas "trädgårdar bestående av olika former av kemiska fällningar". Kemiska trädgårdar uppstår via kemiska reaktioner och fysikaliska processer och ger upphov till upprättväxande strukturer, som påminner om växtplantor. Vanligen används vid dessa experiment olika starkt färgade salter av metaller och demonstreras flitigt i skolkurser i naturvetenskaper. Och varför talar vi om rörformiga strukturer (tuber)? Därför att tuber är grundläggande strukturer i kemiska trädgårdar. Då trädgårdarna växer till sig formas ihåliga strukturer, som kan karakteriseras som tuber (bild på sidan 30).

Vi talar om strukturer som växer. Menar vi med detta att strukturerna är "levande"? När kan vi konstatera att något har ett liv, är levande? Membraner är något som kemiska trädgårdar och livets uppkomst har gemensamt och är beroende av och under dessa två processer skapas membraner på ett sätt, som starkt påminner om varandra. Vår diskussion om livet kan vi fortsätta med citat rörande kemiska trädgårdar, som hittas i boken "Mechanism of Life" skriven av Stephane Leduc.

"Genom osmos eller osmotisk tillväxt kan vanligt förekommande mineraler såsom karbonater, fosfater, silikater, nitrater, och klorider komma att uppvisa former, som påminner om former hos levande ting utan inverkan av en levande organism. Vanligt förekommande fysiska krafter eller processer har förmågan att skapa former, som påminner om dem vi påträffar hos levande varelser, tex slutna hålrum, som innehåller olika vätskor, separerade med osmotiska väggar (membraner), vävnader som i avseende på form, färg, uppkomst och funktion, liknar dem som vi finner i vitala organ… Osmotisk tillväxt, som resulterar i osmotisk vegetation, måste ha varit en mycket allmän process i de urtida haven. Mängder av mineraler och föreningar, som kom i kontakt med varandra, hade möjlighet att producera osmotiska membraner som inte bara föddes utan även utvecklades, upplöstes och dog. Under tidernas lopp, då den levande världen representerades av ting organiserade via osmos, måste miljontals kortlivade former ha uppstått och blivit ersatta av andra under den tidsrymd, som den naturliga evolutionen hade till förfogande.”

Frågan om vad liv är och vad som menas med att vara vid liv, fascinerar vetenskapsmän/kvinnor och allmänheten. En annan intressant fråga är livets uppkomst (the origin of life), var fick livet sin början? Vetenskapligt används termen ”Origin of Life” ofta för att beskriva hur icke-levande materia har omvandlats till levande via processer, som inte är helt klarlagda eller förstådda. Man känner emellertid till att de äldsta formerna av liv har uppstått i de varma källorna (”hydrothermal springs”) som ligger djupt i bottnet av oceanerna. I dessa källors miljö finns alla viktiga föreningar (väte, metan, ammoniak, koldioxid och nitrat) som krävs för att biosyntes skall kunna uppstå. Intressant är att i dessa källor finns samma processer, som verkar i kemiska trädgårdar, till exempel olika gradienter mellan membraner som driver utbyte av elektroner och protoner. Vidare har vetenskapen lyckats visa på förekomsten av reaktioner, som öppnar möjligheten till ämnesomsättning som möjliggör tillverkning av mera komplicerade ämnen, molekyler (autotrophic metabolism). Många frågor kvarstår obesvarade då det gäller livets uppkomst via prebiotiska föreningar. Försök på vägen till svar på några av dessa frågor, kräver noggranna studier av flöden genom kemiska trädgårdar och dess membraner.

Vi inbjuder allmänheten att bekanta sig med detta fascinerande ämne genom att möjliggöra observationer av tuber (eller kemiska trädgårdar) bestående av kalciumfosfat, som växer i en behållare av glas i mitten av bordet. Liksom gräset, som växer på bakgården, kräver tuberna en för dem gynnsam omgivning och näring för tillväxt. I vårt fall består ”myllan” av en gel av biopolymer och ”näringen” av natriumfosfat, som erhålls från biopolymeren. Gelen finns på bottnen av vasen och näringen finns upplöst i vätskefasen i vasens övre del. Tubernas diameter varierar från ungefär 30 till 40 mikrometer (samma diameter som hos vårt hår) och de kan observeras i ett ljusmikroskop.

Jan-Erik: Jag har tänkt mycket över de sätt på vilka jag kan svara på den utmaning, som deltagandet i detta projekt innebär. Jag ville inte göra en illustration av de kemiska trädgårdarna med hjälp av kon-

Photos: Jan-Erik Andersson


EMI
COLINE 80 cm

sten. Likaväl ansåg jag det vara svårt att göra någon slags tolkning av de kemiska trädgårdarna, på grund av den komplicerade kemi och graden av abstraktion, som ligger som bas för dem.

I stället valde jag att göra en *presentation* av trädgårdarna. Mitt mål, och också resultat, blev att söka efter ett sätt där jag framhäver trädgårdarnas skönhet, att sätta dem på en plattform, i detta fall ett bord, som även samtidigt fungerar en plats där kommunikation sker.

Jag har en lång erfarenhet av Bordets kommunikativa egenskaper. I normala fall, åtminstone innan koronan, sker huvuddelen av vår kommunikation kring, över och under ett bord! Med andra ord, vad skulle bättre passa det tema, som Laura Hellstens forskning har, beskrivet i början av denna broschyr!

En annan ide var, att det skulle vara roligt om människor helt slumpvis skulle stöta på vårt projekt, vilket skulle hända om bordet skulle vara placerat i ett helt vanligt kommersiellt café och vara i användning där.

Mitt på bordet skulle en cylinder av glas innehålla den kemiska trädgården. Ingen invecklad, filosofi, eller ett försök att visuellt ”förklara” mycket komplicerade kemiska processer, utan rätt och slätt en plats, som lyfter upp skönheten hos oorganisk tillväxt.

Ursprungligen ville jag göra hela bordet av oorganiska material, men senare beslöt jag mig att göra endast bordsytan av betong, jord och järn och benen tillverkades av återanvänt trä, målade i sex olika gröna nyanser.

Jag delade bordsytan i tre delar (för vilket jag inte har någon egentlig förklaring!). Sedan gjorde jag en form, som lades mot en jordyta i vår trädgård. Betongen hälldes i och när den stelnat blev det spår av jorden i betongytan. Mellan dessa tre betongdelar lade jag smala järnplattor, vilka börjar rosta om man spiller vätska på dem.

Den ruggiga och ojämna betongytan utgör en utmaning för cafébesökaren, som kommer att vara tvungen att söka efter en jämn yta för att placera sin kaffekopp på. En sorts symbol för den osäkerhet vi alla känner för tillfället, angående framtiden för det organiska livet på vår planet.

Anna: Jag har alltid varit extra förtjust i och fascinerad av sådana kemiska reaktion och processer som kan observeras med blotta ögat. Som lärare i naturvetenskapliga ämnen med stort intresse för vetenskapskommunikation, har detta projekt varit ett väldigt spännande och intressant äventyr. Jag har fått möjligheten att vidga vyerna både för min forskning och för min kärlek till naturvetenskapen, något som jag uppskattat väldigt mycket. Det har också varit ett sant privilegium att få ta del av de tankar, som vårt kemiska arbete väcker hos andra människor. På samma sätt har det varit väldigt intressant att följa med Jan-Eriks arbete kring våra kemiska trädgårdar.

Jan-Erik: Jag pratade om vårt projekt med en person och försökte förklara skillnaden mellan det organiska och det oorganiska, genom att säga att organisk kemi handlar om kol-baserade föreningar, vilka utgör byggstenar för allt som” lever” på vår planet, medan den oorganiska kemin handlar om de material och saker som är ”döda”.
Hen blev mycket upprörd och sade att alla stenar är ”levande”. Jag undrar hur gammaldags mina begrepp om kemi och liv är, speciellt nu när vi har trätt in i en posthumanistisk period, då människan inte längre antas vara den mest betydande arten på vår planet.

Jan-Erik, Phat & Anna: Vi önskar nu bjuda in dig, läsare och betraktare, för att dela med dig av dina tankar kring vårt projekt. Kontakta oss, dina vänner eller bara som en tyst diskussion med resten av universum. Vi hoppas du har en möjlighet att ta litet tid för att, genom vårt projekt, njuta av skönheten som finns i världen.

1. Geoffrey J. T. Cooper, Philip J. Kitson, Ross Winter, Michele Zagnoni, De-Liang Long, Leroy Cronin. Modular Redox-Active Inorganic Chemical Cells: iCHELLs. Angewandte Chemie International Edition, 2011; DOI: 10.1002/anie.201105068
2. Leduc, S. The Mechanism of Life. (Rebman, 1911).
3. Yamaguchi, A. et al. Electrochemical CO2 Reduction by Ni-containing Iron Sulfides: How Is CO2 Electrochemically Reduced at Bisulfide-Bearing Deep-sea Hydrothermal Precipitates? Electrochim. Acta 141, 311-318, doi:https://doi.org/10.1016/j.electacta.2014.07.078 (2014).

Photo: Robert Seger

Jag är Jan-Erik Andersson, en visuell konstnär som arbetar brett med installationer, skulpturer, mediekonst, miljökonst och arkitektur. Jag föddes i Åbo, som fortfarande är centrum i mitt liv. Jag bor på ön Hirvensalo i *Life on a Leaf*, ett hus och helhetskonstverk, som också är mitt doktorsarbete vid Bildkonstakademin i Helsingfors.

Jag är mycket intresserad av hur livet och forskning kan integreras i min konstnärliga praktik. Jag har den stora glädjen att åtnjuta statens konstnärspension, vilket ger mig en stor frihet att göra och utforska vad helst jag vill! För tillfället planerar jag ett nytt, hexagonalt stockhus med konstnärliga interventioner.

Jag har en bakgrund i naturvetenskaper (Nat.kand) vid Åbo Akademi, där jag studerade organisk kemi, biologi, botanik och konsthistoria. Jag har också en examen från Åbo Ritskola (nuvarande Åbo konstakademi) samt är doktor i bildkonst från Bildkonstakademin i Helsingfors (Konstuniversitetet), där jag för tillfället är affilierad postdoc forskare. Mitt huvudintresse är hur konsten kan skapa arkitektonisk rymd och hur en samarbetsprocess mellan konstnärer och arkitekter kan se ut.

Mitt namn är Anna Fogde och jag är en glad och nyfiken doktorand inriktad på fysikalisk kemi. Jag kommer från Mariehamn, men är numera bosatt i Åbo, där jag har bott sedan jag inledde mina universitetsstudier. Jag tycker att världen är fylld av fantastiska och spännande fenomen och även om grundskolans lägre klasser sedan länge är avklarade är jag fortfarande barnsligt förtjust i saker som rödkålssaft och såpbubblor (och att trycka på knappar).

I min forskning är jag mest intresserad av sådant, som händer på ytor och i gränsytor. För tillfället undersöker jag egenskaper hos material skapade i gränsytan mellan geler och vätskor. Jag arbetar tillsammans med Tan Phat Huynh, och som han konstaterade i sin presentation, har våra material inte bara intressanta egenskaper utan de är även vackra att titta på.

Jag är också intresserad av att testa gränserna för hur pass enkla material och metoder man kan arbeta med (utan att för den skull ge avkall på resultaten). Utöver att vara kemist är jag nämligen också utbildad ämneslärare och tycker om att söka efter möjligheter till att introducera det jag håller på med i olika undervisningssituationer. Att arbeta med enkla medel och metoder ser jag som en möjlighet till att även praktiskt ta in forskningen till klassrum, utan att stora kostnader och/eller avsaknad av utrustning sätter hinder.

MITT NAMN ÄR TAN PHAT HUYNH från Vietnam. För tillfället bor jag i Åbo med min fru (som är polsk medborgare) och vår 18 månader gamla dotter.

Jag forskar i supramolekylära material och "supra" betyder i detta sammanhang "högre". Dessa supramolekylära substanser, vilka utvecklats i vår grupp, besitter inte bara komplicerade strukturer och funktioner, vilka tillåter dem att användas i medicinsk och miljöforskning, men också en enastående skönhet (kemiska trädgårdar). Vid sidan om min forskning, gillar jag att vara ute i naturen med min familj. Jag gillar också att vara tillsamman med vänner och ta en öl tillsammans.

Photos: Jan-Erik Andersson

The Table and the Tubes

VISUAL ARTIST JAN-ERIK ANDERSSON AND RESEARCHER TAN PHAT HUYNH WITH ASSISTANCE OF RESEARCHER ANNA FOGDE.

This project is a part of *Avtryck i det Okända – Forcing the Impossible*, a multidisciplinary research project led by post-doctoral researcher Laura Hellsten where science and art are combined in order to explore science communication. Within the frames of the project, cutting-edge researchers at Åbo Akademi University meet artists. The scientists get to practice communicating their research outside of the scientific community, and the artists get to interpret and illustrate what they see/hear/touch, using their respective media. Within their different groups the researchers and artists have independently decided if the final presentation is a joint endeavour engaging both the researchers and artist on equal terms or if there is more emphasis put on describing the artistic and research project as parallel tracks.

In the project The Table and the Tubes, the booklet you are currently reading is what was collaboratively created by the researcers and artists to engage with you, the audience. The Table and the Tubes further include a table/ sculpture by visual artist Jan-Erik Andersson and a chemical garden presented in a vase on the table by Dr Tan Phat Huynh and doctoral student Anna Fogde.

Jan-Erik: For me, the question of what life is, what is "alive" has always been of key interest. When I was young in the 1960ties the education in the school never really stressed the fact that many concepts and borderlines are very vague and instead of sharp unquestionable truths, the world is made up of floating spectrums, with endless variation. At least when you give things a closer look, nature produces new variations all the time.

Now when AI (Artificial Intelligence) is questioning the uniqueness of the human "mind", also the origin of life and the border between non-living and living have been questioned. Some researchers talk about "inorganic biology" when they are trying to create self-replicating, evolving inorganic cells, which even can store electricity, just in the same way as organic, biological, carbon-based cells do.[1] In the words of Albert Szent-Gyorgi: "Life is nothing but an electron looking for a place to rest."

It was fascinating to take a first look at the Chemical Gardens created by Phat and Anna to discover the visual beauty of the inorganic, growing structures. Like the organic nature is considered, at least earlier, to hold the ultimate "beauty", also the inorganic structures possess beauty.

Phat & Anna: What are these Chemical Gardens? Literally, they are "Gardens of precipitated chemical forms". A chemical garden is the result of chemical reactions and physical processes that give rise to upwards growing structure that exhibit plant-like features. Usually, metal salts with beautiful colours are used and as a result the experiment is very popular in science classrooms. And why are we talking about tubes? Because tubular structures are a basic characteristic of the chemical gardens. The growing process of the garden makes the structures hollow, and therefore they can be regarded as tubes (page 30).

We are talking about our structures as growing. Does that mean we are considering them to be alive? When can something be considered being alive and living? Chemical gardens and the origin of life share some common elements in the way the membrane is formed. Let us therefore continue our intriguing journey regarding the question of life by taking a look on some quotes discussing Chemical gardens from the book Mechanism of Life written by Stéphane Leduc.

"The phenomena of osmotic growth show how ordinary mineral matter, carbonates, phosphates, silicates, nitrates, and chlorides, may imitate the forms of animated nature without the intervention of any living organism. Ordinary physical forces are quite sufficient to produce forms like those of living beings, closed cavities containing liquids separated by osmotic membranes, with tissues similar to those of the vital organs in form, colour, evolution, and function… During these long ages an exuberant growth of osmotic vegetation must have been produced in these primeval seas. All the substances which were capable of producing osmotic membranes by mutual contact sprang into growth, the soluble salts of calcium, carbonates, phosphates, silicates, albuminoid matter, became organized as osmotic productions, were born, developed,

evolved, dissociated, and died. Millions of ephemeral forms must have succeeded one another in the natural evolution of that age, when the living world was represented by matter thus organized by osmosis".[2]

The question about what life is and what it means to be alive fascinates many, scientist and non-scientist alike. Another interesting question is that of the origin of life, where did life begin? In science the term Origin of life is often used to depict how non-living matter has turned into life by processes still not completely known or understood. It is however known that hydrothermal springs, deep down on the ocean floors, are places where the oldest known life-forms have been found. The environment of the hydrothermal springs have access to all the important prebiotic molecules (hydrogen, methane, ammonia, carbon dioxide and nitrate) needed for biosynthesis to emerge. An interesting feature is that we can also find the same kind of processes here as in the chemical garden systems, with different gradients across membranes that drive fluxes of for examples electrons and protons. Furthermore, scientists have managed to demonstrate reactions that open the gates to autotrophic metabolism.[3] Yet many questions remain to be answered about how life evolved from the prebiotic molecules. And the endeavour to answer some of these questions will call upon further careful study of flows through chemical garden-membranes.

We would like to invite audiences further into this fascinating topic by giving you the opportunity to observe the tubes (or with another name, the chemical garden), here made of calcium phosphates, growing in the vase in the center of the table. Like for grass growing in a backyard, a favourable environment and nutrients are required for the tubes to grow. In our case the "soil" consists of a biopolymer-based gel containing "nutrients" in the form of sodium phosphate. This gel stays in the bottom of the vase, while another nutrient, sodium phosphate dissolved in water, is included in the liquid fraction in the top of the vase. The tubes can vary in diameter from ~30 to 40 micrometer (the same size of the human hairs) and this can be observed under light microscope.

*autotrophic: a living thing that can produce its own food from simple chemical substances such as carbon dioxide.

Jan-Erik: I thought a lot about how to approach this challenge. I didn't want to make an illustration of the Chemical Gardens using art.

Likewise it was very hard to make some kind of interpretation of the Chemical Gardens because of the difficulty and abstraction of the underlying chemistry. Instead, I chose to make a *presentation* of the Gardens, or in this case one garden. My aim was to somehow uplift the beauty of the garden and put it on a platform, in this case a table, which also creates a place where communication takes place.

I have a long-lasting interest in the communication aspects of a table. Usually, at least before Corona, most of the communication takes place around, over and under a table! So, what would fit Laura Hellsten's research theme mentioned in the introduction better! I also thought that it would be great if people would accidentally stumble on our project, as would be the case if the table would be placed in a normal commercial café and be in use there.

In the centre of the table a cylinder made of glass, would hold the Chemical Garden. No complex philosophy, or an attempt to visually "explain" very complex chemical processes, but just a place to honour the beauty of inorganic growth.

Initially I wanted to make the whole table out of inorganic material, but later I decided to make only the surface out of concrete, earth and steel and base it on legs made of recycled wood, painted in six shades of green.

I divided the surface in three parts (for which I have no actual explanation!). Then I made a mould to pour the concrete in, which I put towards the earth to get traces of it on the table surface. Between these concrete parts I inserted iron plates which will start to rust if somebody spills water on them.

The rough concrete would be a demanding surface for the café visitor, who would have to search for a safe (plain!) place to put down the cup. A kind of symbol for the uncertainty we all feel at the moment concerning the future of the organic life on our planet.

Anna: I have always loved and been fascinated by chemical reactions and processes that can be observed visually. And as a teacher with a keen interest in science communication this opportunity to expand the horizons of my research and love of science to new dimensions has been a wonderful adventure. It has been a privilege to take part in the thought process that our chemical work awakens in other people and it has also been very interesting to follow Jan-Erik's work around our chemical gardens.

Jan-Erik: I talked about our project with a person and tried to explain the differences between the organic and the inorganic by saying that the organic chemistry is about coal-based compounds, which make up all "living" things and that the inorganic chemistry is about all "dead" things. She got very upset and said that all stones are "alive". I wonder how outdated my concepts of chemistry and life are, in this posthumanist period, where humans are not supposed to be the primary species on our planet anymore.

Jan-Erik, Phat & Anna: We now invite you, the reader and observer, to share your thoughts around our project. Share it with us, your friends or just as silent thoughts to the rest of the universe. We hope you have the opportunity to take some time and enjoy the beauty of the world through our project.

1. Geoffrey J. T. Cooper, Philip J. Kitson, Ross Winter, Michele Zagnoni, De-Liang Long, Leroy Cronin. Modular Redox-Active Inorganic Chemical Cells: iCHELLs. Angewandte Chemie International Edition, 2011; DOI: 10.1002/anie.201105068
2. Leduc, S. The Mechanism of Life. (Rebman, 1911).
3. Yamaguchi, A. et al. Electrochemical CO2 Reduction by Ni-containing Iron Sulfides: How Is CO2 Electrochemically Reduced at Bisulfide-Bearing Deep-sea Hydrothermal Precipitates? Electrochim. Acta 141, 311-318, doi:https://doi.org/10.1016/j.electacta.2014.07.078 (2014).

Photo: Robert Seger

I am Jan-Erik Andersson a visual artist working broadly with installations, sculptures, media works, environmental works and architecture. I was born in Turku and Turku is still the centre of my universe; I live on Hirvensalo island in the Life on a Leaf house, a total artwork which also is my Doctoral work at the Academy of Fine Arts, Helsinki.

I am very interested how life and research can be integrated in my artistic practice. I am very happy to enjoy the state artist pension, which gives me freedom to explore whatever I want! At the moment I am planning a new experimental hexagonal log house with artistic interventions.

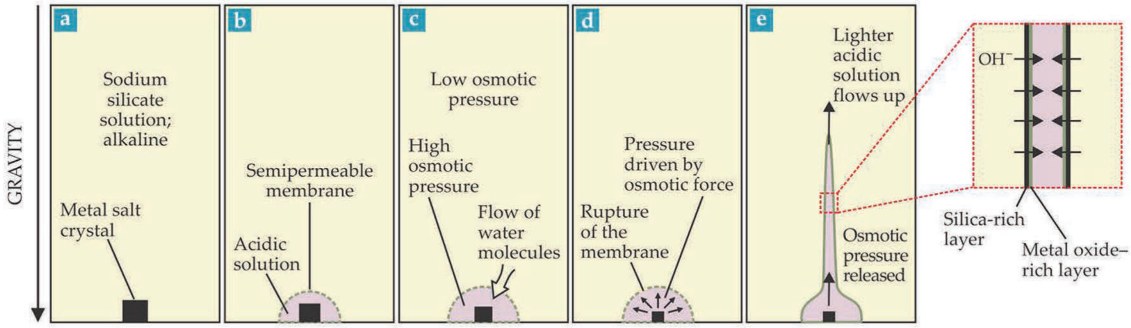
I have a background in natural sciences (BSc) at the Åbo Academi University where I studied Organic chemistry, Biology, Botany and Art history. I also graduated from the Turku Arts Academy and have a Doctorate in Fine Arts (DFA) from the Academy of Fine Arts, University of the Arts, Helsinki, where I am an affiliated postdoc researcher at the moment. My main interest is how art can create architectural space and in the collaborative processes between an artist and an architect.

My name is Anna Fogde, and I'm a happy and curious doctoral student within the field of physical chemistry. I come from Mariehamn on Åland, but I have lived in Turku since the beginning of my university studies. I find the world filled with fantastic and exciting phenomena, and even if my early school years are far away, my childlike enchantment for red cabbage juice, soap bubbles and pressing buttons is intact.

In my research, I'm particularly interested in what happens on surfaces and at interfaces. Currently, I'm investigating characteristics of materials originating from the interfaces of gels and liquids. I'm collaborating with Tan Phat Huynh. Like he notes in his presentation, our materials do not only exhibit interesting characteristics but are also beautiful to behold. I'm also interested in testing the limits for how simple materials and methods one can work with (without compromising results). In addition to being a chemist, I have an education as a subject teacher, and I'm always on the lookout for different ways to introduce what I'm researching into different educational environments. I regard employing simple means and methods as a gateway for bringing research into classrooms without the hindrance of great expense or being reliant on complicated equipment.

My name is Tan Phat Huynh from Vietnam. I currently live in Turku with my wife (Polish citizen) and my 18-month daughter.

My research is about supramolecular materials and "supra" here means "higher". These supramolecular materials developed in our group possess not only advanced structures and functions allowing them to be used in medical and environmental research but also an outstanding beauty (e.g. chemical gardens). Apart from research, I like enjoying nature with my family. I also like to spend time with friends and have a beer together.



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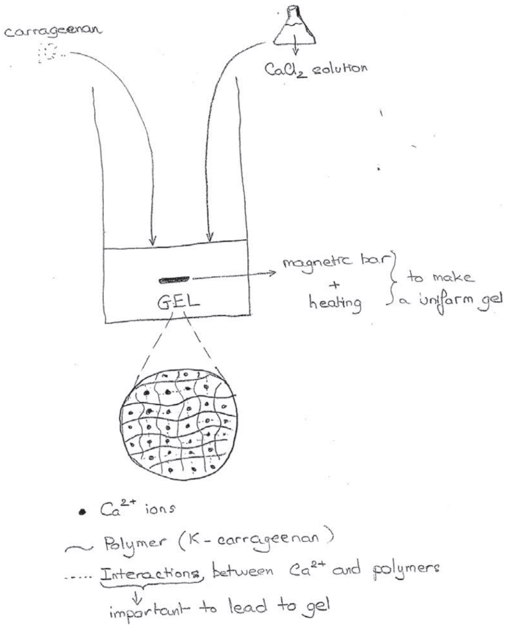

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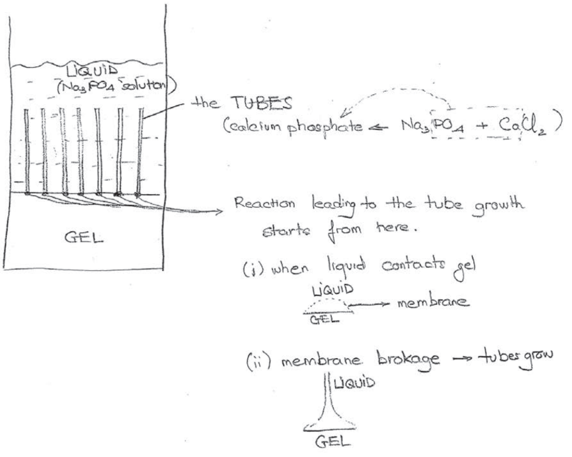

(calcium phosphate ← $Na_3PO_4 + CaCl_2$)

Reaction leading to the tube growth starts from here.

(i) when liquid contacts gel

(ii) membrane brokage → tubes grow

(iii) Tubes only stop growing when there is no difference (chemically) between the inner & outer regions of the tube.

Photo: Pekko Vasantola

Laura Hellsten's Forcing the Impossible reserach project:
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5 Pekko Vasantola

5 J-e A

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