Water purification by adsorption on natural sands

Bachelor Thesis

Water purification
by adsorption on natural sands

Bachelor Thesis
8th of June, 2020

By
Oda Johanna Agdal
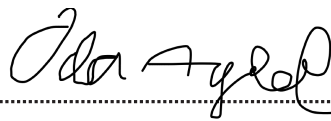
Approval

This thesis has been prepared over five months at the Section for Functional Oxides, Department of Energy Conversion and Storage, at the Technical University of Denmark, DTU, in partial fulfilment for the degree Bachelor of Science in Engineering, BSc Eng.

Oda Johanna Agdal - s174442

....
Signature

08.06.2020
....
Date

Abstract

Poor water quality directly impacts health and water pollution is an increasing problem worldwide. New types of pollutants are emerging, and many water treatment facilities are not adequately equipped to handle them. In this project, the ability of sand to purify contaminated water has been investigated in different scenarios. The focus has been on three main aspects and their effects on sand adsorption; sand treatment, water type and sand origin. The sand was analysed using x-ray diffraction and scanning electron microscopy (SEM), and sand adsorption was calculated using spectrophotometer data on sample absorption measured over time. The adsorption tests were conducted in a container with a thin layer of sand at the bottom and a contaminated water solution with 5ppm of different industrial dyes.

In terms of sand treatment, the sand was dried under different temperatures (up to $500°C$) to see if heat treatment could be used to recycle the sand. Some dyes were absorbed a little better with the heat-treated sand, some a little worse - but on average across all tests, the difference was less than 5% when compared to the dried sand. Heat treatment was accepted as a suitable way to recycle the sand for adsorption. Regarding sand type, sand of both lake and sea origin was tested. The SEM and x-ray diffraction showed that both samples were mainly silicate, but that titanium and iron that are known for their adsorption abilities, were more present in the lake sand. However, the sea sand proved to have better adsorption abilities, likely due to the superior uniformity. Lastly, the experimental comparison of water types included demineralised-water and seawater with two industrial dyes and gave a strong correlation of 0.97 - suggesting that the data can be extrapolated. However, a similar study tested with more dyes found that this strong correlation did not hold for all dyes - just the two tested. The results regarding water types are, therefore, inconclusive.

Sand filters are still used in industrialised countries like Norway and Denmark, but then as part of multi-stage treatment or in simple drainage wells. The findings found can be relevant for these commercial sand filters.

Preface

The bachelor thesis describes water purification through sand adsorption in various scenarios. The supervisor was Jean-Claude Grivel from DTU Energy Conversion and Storage. Firstly I would like to thank him for his general guidance and help. I would further want to thank him for letting me use his previously collected data as the university locked down as a result of COVID-19, and his flexibility when the scope of the thesis had to be altered for the same reason. Finally, I would like to thank Trond Lohne and Jesper Furdal for resourceful interviews.

Acknowledgements

Contents

1   Introduction

Poor water quality directly impacts health. Both by limiting access to clean water, and by increasing water-related health risks. Water quality remains a problem, both in the developed and developing nations, and UN sustainability goal number 6 goes to ensure clean water and sanitation for all before 2030 [39]. Three out of ten people do not have access to safe drinking water, and six out of ten people do not have access to safely managed sanitation services on a global scale. Water use is also increasing by 1% annually since the 1980s and expected to keep rising at a similar level the next 30 years [41], making water treatment technology increasingly important. Sand filtration is a globally available and cheap way to purify water, but further research on how to combat new and rising water pollutants is needed. This thesis focuses on the adsorption efficiency of sand filtration and evaluating the potentials to remove emerging pollutants from water using simple sand filtration. To do this, water samples polluted with different industrial dyes in various scenarios were investigated.

1.1   Emerging Pollutants in Europe

Water pollution is also a problem in industrialised nations. In the European freshwaters and coastal regions, the presence of emerging pollutants (EPs) are now at quantities that have made the EU science board call for urgent action already in 2015 [1]. Heavy metals also remain a problem. This increase in pollutants represents a potentially serious threat to both human health and eco-systems [14]. EPs are defined as synthetic or naturally occurring chemicals that are not usually monitored, but that have the potential to enter the environment and cause known or suspected ecological and/or human health effects. According to the NORMAN network (www.norman-network.net/), there are now over 900 EPs listed in the European aquatic environment. Problematically, most national surveys on water quality tend to use parameters for water quality assessment that often exclude EPs. For some of the known hazardous EPs, that are within the parameters, the normal detection levels are too high to allow proper risk assessment [14].

However, alongside the increase in polluted water, public awareness and industrial focus are also raising. Already in 2008, the New York Times had an article with the apt name of "A Tall, Cool Drink of ... Sewage?" and around the same time, Sweden developed a national classification system based on the risk and (or) hazard of active pharmaceutical ingredients. Just in 2018 the Norwegian energy company, Norsk Hydro, lost over 2 billion kroner when contaminated water was released from their alumina plant into an unlicensed river in Brazil. The contaminated water reached the drinking supply in hundreds of houses.

Globally, it is estimated that around 10% of all illnesses can be eliminated by improvements in drinking-water, sanitation hygiene and water resource management, making water technologies good business. It follows that globally speaking, clean water technology is found to have a $3-4 dollar return on every dollar invested [46].

1.2   Water Purification Using Sand Filters

There are many ways of purifying water in use today, but sand filters that clean the water through filtration are one of the oldest and simplest. Filtration is simply the operation that separates a solid from a fluid through a filter medium with a complex enough structure so that only the liquid is allowed to pass. As the fluid, water in this case, passes through the medium, which is sand, contamination particles adhere to the surface of the sand in

a process called adsorption. The process leaves the water free of these particles when having passed through. This might sound simple enough, but the physical, chemical, and bacteriological improvement in water quality when going through a sand filter, is better than any other single process [7].

1.3 Thesis Focus

For this thesis, the focus of inspection will be the gravitational slow sand filter, and its performance in different scenarios to deduce what effects its ability when removing emerging pollutants from water. This will further give insight into how, and in what way, this technology can be applied when dealing with the new pollution issues arising.

In total, three different aspects will be evaluated. First, the sand will be investigated in terms of treatment, then, in origin. Finally, testing will be conducted on different types of water. All adsorption tests will be made on water solutions containing dissolved industrial dyes. The sand will be used in both dry state and after heat treatments, whose purpose is to remove organic surface material. Heat treatment could potentially be used to recycle the sand after adsorption if the adsorption shows to be unaffected. The water used in the tests will be demineralised water and natural seawater, and sand originating from both freshwater lakes and sea will be used.

The different aspects of investigation have been formulated into three different hypotheses:

A. Heat treatment of sand will not affect adsorbing abilities within the tested range.

B. The sand will show similar purification properties when used in seawater and demineralised water.

C. Sea sand has better adsorbing abilities than lake sand.

Sand characterisation is performed employing scanning electron microscopy (SEM), elemental analysis (EDS) and X-ray diffraction. Continuing, the adsorption efficiency is analysed using the techniques mentioned above together with UV-Vis spectroscopy.

Finally, through conversations with professionals in the water treatment industry from Norway and Denmark, the relevance of this work for the industry will be discussed.

2 Theory

In this chapter, the relevant and necessary theory needed in this project is displayed. The primary purpose of this chapter is to lay a basis for the analysis and interpretation of results later presented.

2.1 Sand

Defined in the Glossary Terms in Soil Science as: *(i) A soil particle between 0.05 and 2.0 mm in diameter. (ii) Anyone of five soil separates: very coarse sand, coarse sand, medium sand, fine sand, or very fine sand.(iii) A soil textural class. [3]* Clay, as a comparison, is a soil consisting of particles of less than 0.002 mm in diameter.

The two sand types handled in this project are sea sand and lake sand. Lake sand is from the freshwater lake Avnsø, one of the cleanest on all of Zealand [43] and with a natural sand bed. The sea sand is from Risø in Roskilde fjord. As no relevant literature has been found to describe the differences in these two types in a general way, a study of the sand samples applied for this project will be done in section 4.1.

2.2 Pollutants

There are many sources of EPs in the European freshwaters and coastal regions. The growing use of pharmaceuticals, due to population growth, ageing and overall increased wealth, has made them represent a significant part of the EPs discharged. The NOR-MAN network also mentions pesticides, disinfection by-produce, wood preservation and industrial chemicals as prominent classes. The discharge of these pollutants mainly reach coastal and sea waters as ultimate sinks after being discharged by municipal wastewater treatment plants (MWWTPs). A study made in the Warta River in Poland demonstrated the impact of MWWTP discharge on water bodies as all samples taken found pharmaceutical waste products at several ng/L [45].

An estimate of the Baltic Sea states that MWWTPs release 1.8 thousand tons of pharmaceuticals per year into the environment. Out of the 118 assessed pharmaceuticals only nine were removed during the treatment process with efficiency above 95%. Almost half of the pollutants were only partially removed, with an efficiency of less than 50% [40]. The conventional MWWTPs are not equipped to remove the stable low-concentrations that the pharmaceuticals represent, typically from ng/L up to µg/L [21].

Industrial dyes are often used as pollutants in research regarding sand adsorption - this is also what has been done for this project.

2.3 Slow Sand Filter

Sand filters have a long history of purifying water and are generally divided into two main subcategories; the rapid and the slow. The slow sand filter dates back to the 19th century United Kingdom and is nowadays found in smaller communities and developing nations with land and labour to spare. Rapid sand filters is a newer technology and more often seen as part of modern multi-stage filters in developed countries. As a part of multi-stage treatments, the sand filter also helps remove the solids formed during pre-treatment, as coagulation or flocculation. Higher labour costs and rising land prices often make slow filters economically disadvantageous in these regions now. The rapid filters are compact

and land efficient, but expensive. In the slow filters, the rate of filtration is down to one-twentieth that of a rapid filter [29]. The rapid filter uses coarser sand, whereas the slow filter uses finer sand and is more sensitive to changes in water quality.

Normally, a filter chamber is filled with several layers of sand, the coarsest at the bottom and the finest at the top. The water is then supplied at the top, passes through the sand where sand corns block bigger particles, and smaller particles can be adsorbed on the surface before it reaches some support and under-drainage below the sand at the bottom. The surface adsorption is mainly due to the van der Waals forces. A pump or gravity can cause the flow of the sand. In Figure 2.1, one can see an example of the gravitational principle.

The slow sand filters, when being used commercially, are 1-2 meters deep. The normal cleaning rate is 200-400 L/h per square meter and is primarily used to clean surface water. Where the rapid filters only filtrate by physically blocking particles in between sand grains, the slow sand filter also filtrates by growing a biological filter. This filtering layer, often called schmutzedecke from German, grows naturally as some bacteria are too big to pass through the sand, and increases the ability to capture the finer particles [29]. The mechanical stopping of the microorganisms is not as efficient as the schmutzedecke, given that the later has been allowed enough time to grow. Growth time for maximum efficiency is about one to two weeks [7]. According to Clark,[7], there are only two other variables that can alter efficiency in the same magnitude as the schmutzedecke, the size and uniformity of the sand particles. Bigger sand grains are, logically enough, more efficient, but also let more particles through. Non-uniform tends to clog, as the smaller sand corn can block the space between the bigger sand corn once water flows through. Colder temperatures negatively affect as bacteria activity decreases with temperature, and this worsens the performance of the filter, to help prevent this, a closed box could be constructed as the filter chamber. Research also suggests that the filter is best maintained with a constant flow of water. The constant flow would also provide nutrients and oxygen to the bacteria in the schmutzedecke. To ensure this constant flow, the water reservoir is often placed above the filter; in that way, a naturally provided pressure head to push the water through the filter occurs. As mentioned earlier, electricity can also be used to pump the water through, but in this thesis, the gravitational filter is the focus.
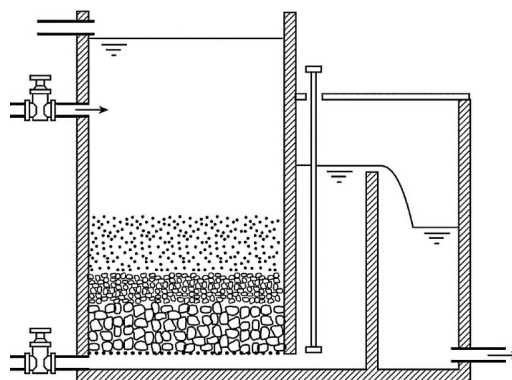

Figure 2.1: Principle of a slow sand filter [18]

With gravitational filters, the water is supplied and can remain in the pool for hours before it passes through the sand bed below. This pause in water flow allows bigger particles to separate and settle. When it passes through the sand bed below, several purification

processes takes place, as described before. There are several advantages with the slow gravitational filter; most of them related to the simplicity of the design. The fact that there is no need for chemicals, electricity, import of materials or intricate skills to maintain a functioning filter, together with a long lifespan, is what makes this a cheap and accessible way to treat water. Disadvantages of the filter are requirements of significant areas of land, constant water flow, regular maintenance and that minimal water quality before pre-treatment is necessary. For this project, all tests will last for too little time to allow a schmutzedecke to grow, which is why this biological layer will not be assumed to be a contributor to adsorption.

2.4 Dyes

Dyes are color agents often used in research to test the adsorbing abilities of sand when it comes to dealing with pollutants. Experiments were made with a total of 5 compounds, that all are organic and used in industry.

Brilliant Blue, BB	$(C_{45}H_{45}N_3O_7S.Na)$	first clothing dye, later dyed protein
Brilliant Green, BG	$(C_{27}H_{34}N_2O_4S)$	dyes silk and wood
Phenol Red, PR	$(C_{19}H_{14}O_5S)$	pH indicator
Rhodamine B, RB	$(C_{28}H_{31}ClN_2O_3)$	tracer dye in water and biomarker
Methylene Blue, MB	$(C_{16}H_{18}ClN_3S)$	medicine and dye

BB,BG and PR source [8], RB source [24] and MB source [22].
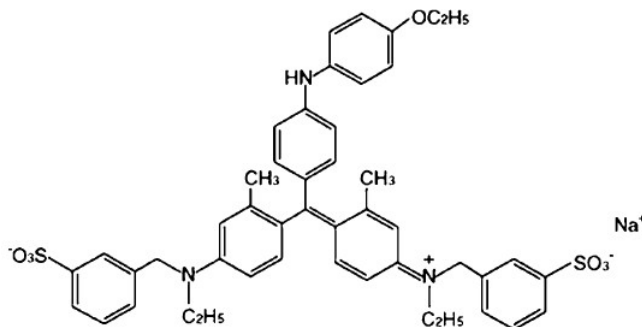

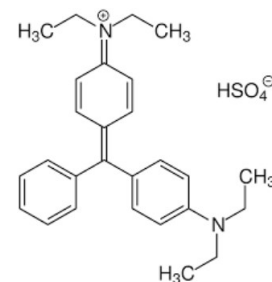Figure 2.2: Molecular Structure of Brilliant Blue [23]

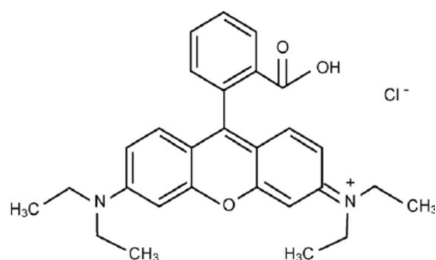Figure 2.3: Molecular Structure of Brilliant Green [27]

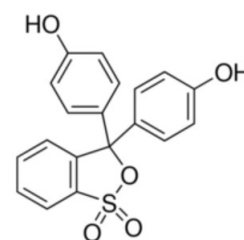Figure 2.4: Molecular Structure of Rhodamine B [24]

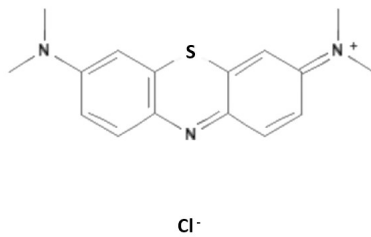Figure 2.5: Molecular Structure of Phenol Red [35]

Figure 2.6: Molecular Structure of Methylene Blue [4]

Many organic compounds, including the 5 dyes discussed here, have conjugated double bond systems. Conjugated double bond systems are molecules where every other bond is a double bound. When looking at the dyes' molecular structures in figs. 2.2 to 2.6, the conjugated double bond systems can be spotted as the hexagons with every second line drawn double.These conjugated double bond systems have a significant influence on peak wavelengths and absorption intensities [34], which will become relevant when using absorbance over wave length data collected from the spectrophotometer. The spectrophotometer data collection is explained in section 2.6. The tendency is that the larger the conjugated system, the larger the absorption and the longer the peak wavelength. As one can see in the molecular structures, these compounds all have rather large conjugated systems (minimum of 3), which makes them have peak wavelengths in the visible light region from 400 to 700nm and makes them suitable as dyes.

The different colours of the dyes; blue, green and red, also give an indicator for wherein the visible region they peak in their absorption. As they appear to the human eye with a specific colour, the compounds must absorb the wavelengths of the complementary colour. The visible spectrum goes from blue - green - yellow - orange - red as one goes from shorter (380nm) to longer (740nm) wavelengths. This indicates that PR and RB will have the lowest wavelength peaks, and BB, MB and BG the highest wavelengths of the dyes. However, it is essential to keep in mind that other factors, such as functional groups, also affect the absorption peak, pH, charge and shade of the colour.

The reason that large conjugated bonds tend to have peaks on the left, low wavelength, region, can be explained with Planck's Law. Planck's Law states that: $E = \frac{hc}{\lambda}$, in other words, the energy needed for a photon to excite an electron is inversely proportional to wavelength. The electron configuration in larger conjugated systems makes the electrons more affected by low-energy photons. As the electrons in the dye absorb more at low-energy, the peak wavelength will be in the higher range.

2.5 Water

Tests were run with two different types of water, demineralised water (DI water) and saltwater. DI water is a common form for purified water often found in labs and used in experiments. It is chemically treated to have mineral ions like sodium, calcium, iron, chloride, sulfate, and copper removed. It's often used in experiments as it's purity removes extraneous factors or background noise. Saltwater was chosen as a real-life implementation of sand filters would deal with non-purified water, making it exciting to look at this element. The saltwater was collected in the Roskilde fjord and, as it is unprocessed water from a natural source, it will contain living microorganisms, including bacteria and algae.

As the water is from the sea, it will also include roughly 3% salt in the form of sodium chloride ions and have a slightly alkaline pH, for Roskilde fjord, it is about 8.2 [15]. DI-water is somewhat acidic.

2.6 Instruments

In total, 3 different instruments were used; the spectrophotometer, x-ray diffraction and SEM. The instruments will be presented here so that data collection can be understood and eventual sources of error can be identified.

Spectrophotometers are an obvious choice when investigating the absorption of chemicals in a water solution. X-ray diffraction and SEM are not tools to look at absorption, but rather to investigate the sand samples. Table 2.1 gives an overview.

	Spectrophotometer	X-ray diffraction	SEM
Data output	Absorbance over wavelength that can be used to find concentration.	Diffraction peaks that can be used to identify minerals in sample.	Electrons interaction with a sample creates images of topography and composition.
Measurement technique	Sends photons of specific wavelengths through the sample into a detector.	An x-ray beam is sent onto the sample and diffraction is recorded through a range of angles.	Electrons are shot onto sample. Secondary and back-scattered electrons along with x-rays from excitation are detected.
Application	Dye absorption over wavelength.	Sand Analysis.	Microscopy and elemental analysis.

Table 2.1: Overview of Instruments and Their Application

2.6.1 Spectrophotometer

A spectrophotometer is an instrument that measures the absorption of a sample, often as a function of wavelength. Depending on the wavelength of the photons, the sample inserted in the spectrometer absorbs different amounts of energy. This variation of energy absorbed, in terms of electron excitation, is the absorption spectrum. For these tests, a UV-Vis-NIR spectrometer has been used, giving a wide range of wavelengths from 200-1100nm across the electromagnetic field. The UV range is defined from 200-400nm, the visual range from 400-765nm and the infrared from 765-3200nm.

The spectrophotometer functions by sending light, like that from a halogen LED, through a monochromator. The monochromator is two slits separated by a diffraction grating, like a prism. The first slit makes sure the light photons are travelling on parallel pathways. The prism then splits the light so that each wavelength of photons is travelling to different places in space to make sure that only one chosen wavelength goes through the second slit, and through the sample into the detector. See Figure 2.7 for a simple illustration.
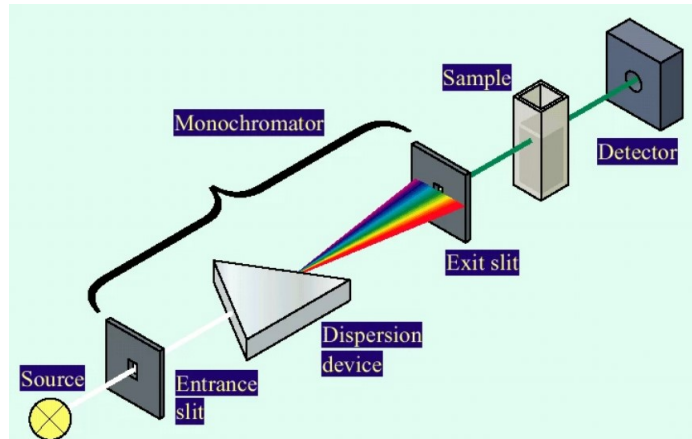
Figure 2.7: Single Beam Optical Design for a UV/Vis/NIR [33]

2.6.2   X-ray Diffraction

X-ray diffraction is also an important tool as it can be used to identify what phases are present in a mixture, like sand. The basic method of X-ray diffraction has not changed since it was invented more than a century ago and refers to the process of sending x-rays through a sample and into a detector. The x-ray device used here is however of a newer type that does not send x-rays through but uses reflection diffraction. The two models share that both x-ray beam and detector gets rotated, such that the samples diffraction is recorded through a range of angles. The diffraction occurs when the x-ray beams are scattered by an array with long-range order and produces constructive interference. A simplified model can be seen in Figure 2.8.

A long-range order means good periodicity of the molecular placement within the crystal structure. The conditions necessary for diffraction can be found and each plane in the crystal will only diffract the light into the detector at these particular angels. These angles will give peaks when running the test. High peaks mean high electron density, and their placement is periodic. Using these diffraction peaks, the minerals the sample consists of can be identified.
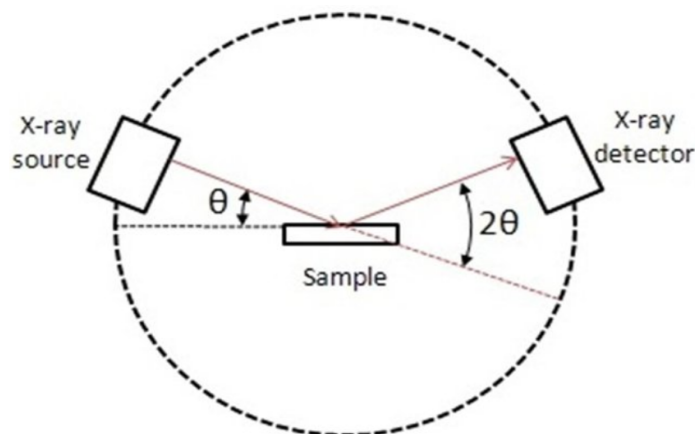

Figure 2.8: Simplified Schematic of an x-ray Diffraction Instrument [2]

2.6.3   Scanning Electron Microscope

The Scanning Electron Microscope (SEM) sends an electron beam down onto a surface to create a detailed picture. As the electrons interact differently to the materials it is shone upon, the image created can also say something about the topography and composition. Due to the high energy of electrons, this type of microscope can create magnifications up to approximately 30,000X the naked eye [37]. For this project the magnifications of 40,1000 and 2000 were used.

SEM works by sending electrons out through an electron gun before an anode accelerates them. The electrons are released from a filament, often a very narrow tip of tungsten, by either heat or an electric field. They are accelerated through the anode as both the anode and the electrons are negatively charged, which makes the anode repel them. After acceleration, the electrons are focused by magnetic lenses - to make sure a very narrow beam of electrons hit the sample.
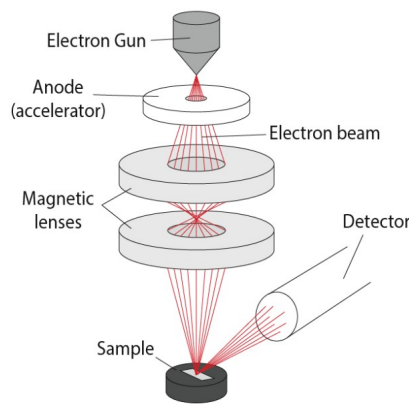
Figure 2.9: Schematic Picture of a SEM [5]

There are three main signals to get from a SEM.
1. Secondary electrons that create an image of the surface structure. Secondary electrons are what you call when the incoming electron takes the place of one in the sample which is then caught by the detector.
2. Back-scatter electrons give insight into the elemental composition, both the crystallographic structure and the chemical position. These images emerge by the electrons that are bent by the nucleus of the atoms in the structure.
3. X-rays that show the elemental analysis. These pictures are made from photons released by electrons in the sample that were excited by the incoming electrons and then fall back to place.

2.7   Equations and Laws

2.7.1   Beer Lamberts Law

Beer Lamberts Law is central when working with adsorption and spectrophotometers as it relates the length and concentration to absorbance with the use of the extinction coefficient [12];

$$A = \varepsilon \cdot l \cdot C. \tag{2.1}$$

Where A is the absorbance value at peak wavelength, ε is the extinction coefficient [L cm^{-1} mol^{-1}], l is the length travelled [cm], and C is the concentration [mol L^{-1}]. As the most standard unit for concentration, ppm, simply means part per million or mg/L, one achieves the concentration needed for Beer Lamberts Law by using the molar mass of

the compound of investigation.

The extinction values are dependent on wavelength, and it is important to make sure the wavelength corresponds to that of investigation or absorbance value. The relevant values for the extinction coefficients can be seen in table 2.2.

Dye	Wavelength [nm]	Extinction Coefficient ε [L cm^{-1} mol $^{-1}$]	Molar Mass [g mol^{-1}]	Source
BB	588	$1.05 \cdot 10^5$	792.85	[38]
BG	624	$1.3 \cdot 10^5$	457.6	[30]
RB	554	$1.08 \cdot 10^5$	792.85	[19]
MB	664	$9.5 \cdot 10^4$	319.85	[22]

Table 2.2: Extinction Coefficent Table

2.7.2 Adsorption Coefficent

Ad is the percentage absorbed, C_0 is the concentration at time zero and C_e is the concentration now [28];

$$Ad(\%) = \frac{C_0 - C_e}{C_0} \cdot 100. \tag{2.2}$$

When finding the values for concentration, it is helpful to take values at the same wavelength, if the concentration is found using Beer Lamberts Law.

2.7.3 Correlation Coefficient

This is a value indicating the strength of a relationship between two samples and takes a value from -1 to 1. At -1 the two samples will have a strong negative correlation and at +1 they have a strong positive correlation. If the coefficient is 0, there is no correlation between the two samples. The equation is as follows [6].

$$Cor = \frac{\sum(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum(x_i - \bar{x})^2 \sum(x_i - \bar{y})^2}} \tag{2.3}$$

Where x_i are the values of the x-sample, $\bar{x}$ is the mean of the x-sample, y_i are the values of the y-sample and $\bar{y}$ is the mean of the y-sample. This calculation also exists as a built-in function in R-studio called "cor".

A positive correlation means that the two samples move in the same direction - as one increases, the other also increases. A negative correlation means that they move opposite to the other - as one increases, the other decreases.

3 Method

There are three main aspects regarding sand adsorption that are investigated for this project; sand treatment (dried and heated), sand type (lake and sea) and water type (fresh and salty). These will be studied in different test scenarios using the instruments described in the previous chapter. Here, the method used to collect, prepare and carry out the experiments is presented.

During preparation for the experiments, the first thing that was done was the collection of the sand. In the first round, the collection was done at Avnsø lake. The second round of sand collection took place at Risø in Roskilde fjord. Both sand samples are assumed to be all-natural. At Roskilde fjord, some seawater was also collected. The Avnsø sand will from now on be referenced as lake sand, the Roskilde fjord sand as sea sand and the Roskilde fjord water as seawater. All three samples were collected at the shore by thesis' supervisor in fall 2019 and kept in a secure plastic container. After collection, the samples were brought to DTU's facilities at Risø for testing. Using x-ray diffraction and SEM, the sand samples were investigated to give some insight to compounds, uniformity and differences. The results of these tests will be explained in section 4.1. Each sand sample was then first sieved, to remove bigger stones and improve uniformity, by using a standard kitchen sieve with mesh holes of about 1x1mm as the one showed in Figure 3.1. After sieving, the sand was split into different parts for treatment. Half of the sea sand was dried at room temperature, and the other half was heat-treated at 140 °C for 1h to remove biological implications in the experiments in an oven. The same was done to the lake sand, except for a little part that was heat-treated at 500 °C. These biological implications could be organic surface material that could grow into this schmutzedecke mentioned in the introduction chapter. This biological activity could both cause clogging in terms of the microorganisms getting stuck in between sand grains, or increase efficiency through biological digestion. The dyes were then tested in several sessions. The base case, or first experiment, was with the dried and 140 °C heat treated lake sand, in DI water. Then variations were done to look at how changing the water, the sand type or sand treatment would affect the adsorption of the different dyes. All the experiments of the same case (sand of the same type and treatment and same water) were run at the same time, so at the most, there were 4 different containers. The "smallest" test series ran consisted of 3 containers. In total there were 4 experiments ran to address the three hypotheses.

For testing, the sand samples under investigation were placed in containers, size 5x7cm^2, with water, such that the concentration of dye was approximately 5ppm. The container had 2mm of sand at the bottom, followed with the water of about 40mL. For testing, a 1x1cm

Figure 3.1: Example of Mesh Strainer Used for Sieving

cuvette was filled with the water and used in the spectrophotometer. Each container had a specific test cuvette belonging to it to avoid additional uncertainties.

After the test containers have been prepared, each container was put in the spectrophotometer to measure absorbance. The absorption spectrum was measured from 200 - 1100nm for all tests, using the spectrophotometer. For roughly 7h, the absorption spectrum was measured regularly, between 9 - 13 times. The instrument saved data onto a USB stick.

Timeline, Experiments Overview with Hypotheses and Glossary

A figurative timeline of how the activities took place could be:

- Sand collection at Avnsø

- Sand and seawater collection at Risø

- Sand analysis

- Experimentation, which includes exploring uncertainties

There was a total of 4 experiments taken on:

Experiment 1: dried and 140°C heated lake sand for BB, BG, RB and PR in DI water

Experiment 2: dried, 140°C heated and 500°C heated lake sand for MB in DI water

Experiment 3: dried and 140°C heated lake sand for BB and BG in seawater

Experiment 4: dried and 140°C heated sea sand for BB and BG in DI water

The four different experiments, which will be further referred to as Experiment 1-4, are linked to the hypothesis in the following way:

Experiment 1,2,3 and 4.	Experiment 3.	Experiment 4.
A. Heat treatment of sand will not affect adsorbing abilities within the tested range.	B. The sand will show similar purification properties when used in sea water and demineralised water.	C. Sea sand has better adsorbing abilities than lake sand.

Table 3.1: Link Between Hypotheses and Experiments

The abbreviations used in the next two chapters are presented in Table3.2. For example, "BG dried" is Brilliant Blue in a container with sand dried at room temperature. For experiment 2 where there are different temperatures of sand treatment, the temperature has been specified.

BG	Brilliant Green	**BB**	Brilliant Blue
RB	Rhodamine B	**PR**	Phenol Red
MB	Methylene Blue	**DI**	Demineralised

dried	room temperature dried	**heated**	140°C heat treated sand

Table 3.2: Glossary

4 Experiments and Results

Before displaying the experimental results of Experiment 1,2,3 in sections 4.3-4.6 two preliminary results are presented as foundation. First an investigation of the sand samples is conducted. Second, a display of how the water absorption noise was removed.

4.1 Investigating the Sand Samples

Both the lake and sea sand was set up in an x-ray diffraction device for mineral composition analysis. The preparation was the one used for the filtration tests, where the sand was sieved and dried. The device used a technique similar to the one explained in the previous chapter. Figure 4.1 and 4.2 shows the output of the test.
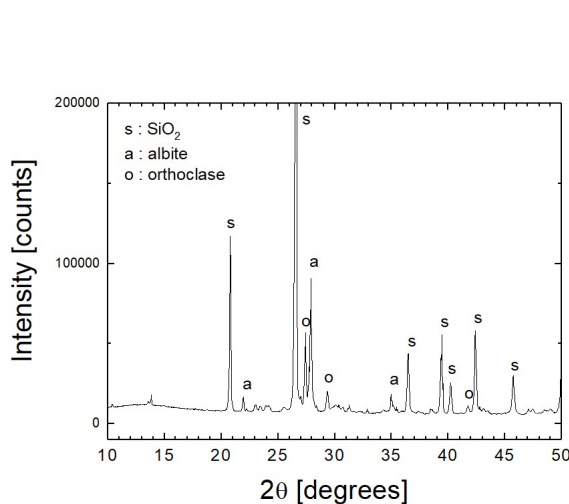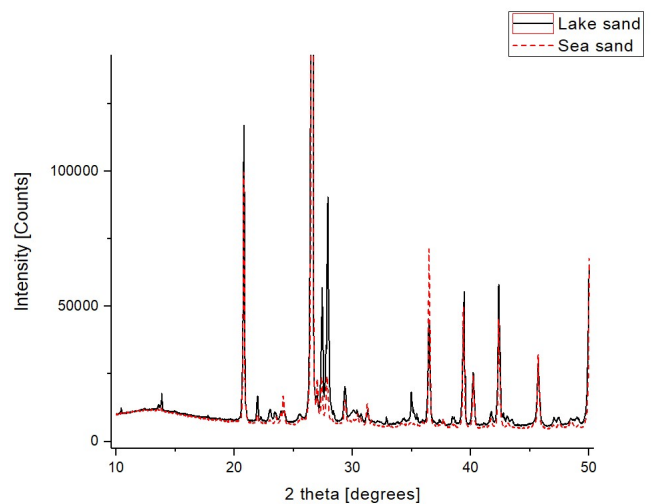

Figure 4.1: X-ray Diffraction of Lake Sand

Figure 4.2: X-ray Diffraction of both Land and Sea Sand

In the right Figure, the elemental analysis of the process showed that the lake sand consists of 3 different compounds - the most present being silicon-dioxide (SiO_2), but also albite and orthoclase. Silicon-dioxide, or silica, is typical to find in natural sand. Albite and orthoclase are both minerals that in pure form also consist of silicon and oxygen, $NaAlSi_3O_8$ and $KAlSi_3O_8$ respectively. The diffraction comparison figure shows that the compounds in lake and sea share many peaks, meaning that the sands consist of some of the same compounds. Especially the peaks for Silicon-oxide are shared by both sea and lake sand. However, when comparing closer, the peaks of both albite and orthoclase are not present in the sea sand. There was also a visual difference in the sand as the lake sand had iron-titanium containing grains in it; this was not the case with the sea sand. More on this later.

Several SEM analysis tests were undergone for both samples as well. In Figures 4.3 and 4.4 a picture of the lake sand, 40 times magnified, and the following elemental analysis from the SEM too can be seen. Similarly, in Figure figs. 4.5 and 4.6, the same can be seen for the sea sand sample. These tests were taken before sieving, but the biggest grains were taken out for practicality.

When comparing the SEM pictures, the sea sand comes off as more uniform - which could increase adsorption abilities. The elemental analysis, more detailed than the one from the x-ray diffraction, sheds light upon what elements are present in smaller amounts. Here iron, titanium, potassium, calcium and sodium are present in both sand types, and chlorine is the only element (found in sea sand) that is not shared between the two. This chlorine could come from naturally dissolved sea salt, sodium chloride.

Although the other elements are shared, they are in different amounts - titanium, iron and calcium are more present in the lake sand, potassium and sodium are more present in the sea sand. There are many examples of studies where iron is added to sand, often as a coating, to increase adsorption [32]. The same goes for titanium, which has shown good adsorption abilities, by itself or alongside iron [9]. An elemental analysis for titanium,
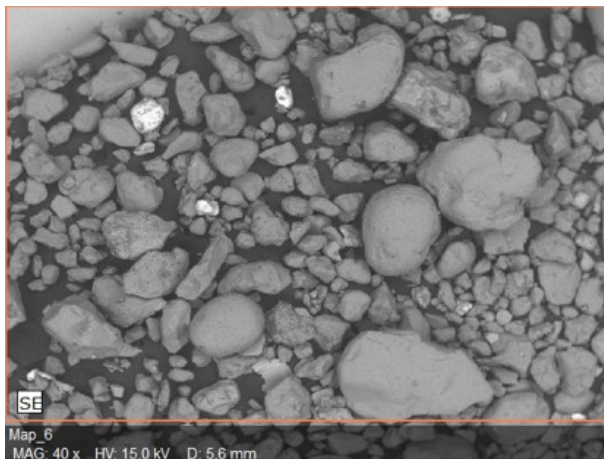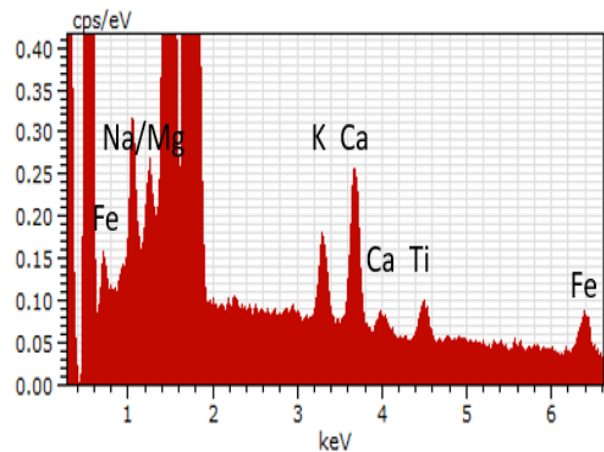

Figure 4.3: SEM Picture of Lake Sand. Mag 40X.

Figure 4.4: Elemental Analysis Over the Whole Picture in Figure 4.3
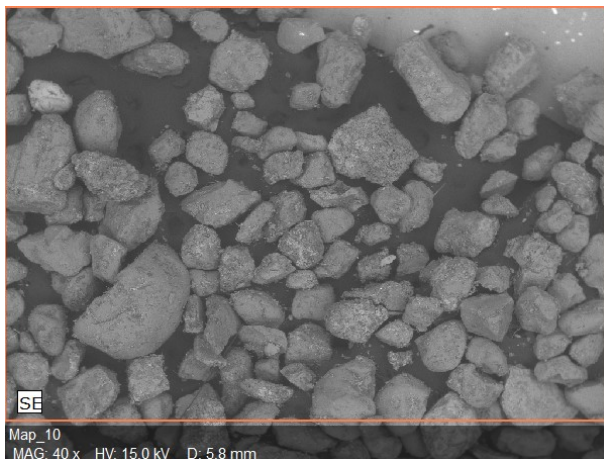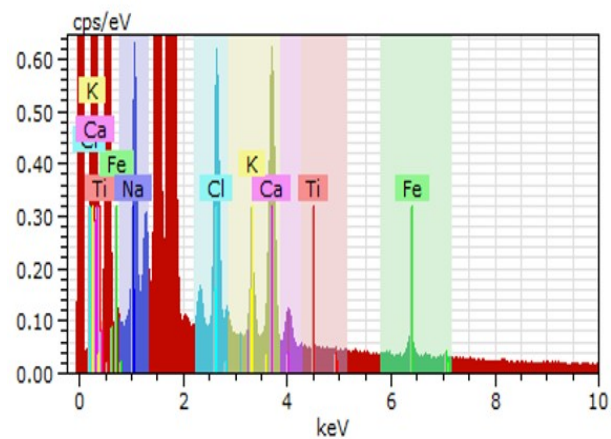

Figure 4.5: SEM Picture of Sea Sand. Mag 40X.

Figure 4.6: Elemental Analysis Over the Picture in Figure 4.5

iron, potassium and calcium was also conducted on the lake sand. The test revealed that there was a big difference in the purity of the stones - some looked pure, others were mixtures. This was true across all the four minerals. The sea sand looked less pure, but fewer tests were done.

When investigating the lake and sea sand at higher magnifications - porous structures,

seemingly of dead microorganisms, were found. Fossilized snails or shellfish turn into small porous patches of Calcium Carbonate ($CaCO_3$) over millions of years and, especially for the lake sand, seem to have rather big surface areas that look good for absorption. The elemental analysis also showed that there were more significant amounts of calcium in the lake sand.

The fact that these elemental and mineral composition analyses all were made before the sand was sieved adds some uncertainty. One side of this is the lack of insight which is reached about how fine the sieving was, which makes it difficult to make a certain statement on uniformity. There is also a possibility that the big grains that would be taken away in sieving all consist of similar compounds and that the elemental analysis' therefore becomes imprecise.

4.2 Removal of Water Absorption Noise

All tests conducted included the use of containers, cuvettes and water. As the testing was done in the cuvettes, it is potential differences in the cuvettes that need to be investigated. The goal of this preliminary test is to eliminate possible differences in the cuvettes that could affect absorption patterns and remove the noise of water absorption. For this test, the cuvettes only held clear water to spot potential differences and eliminate background noise. In Figure 4.7, the four cuvettes were filled with deionized (DI) water. Some individual differences can be spotted, but in general, the normal water absorption peaks at 600nm and 1000nm can be spotted. In the Figure beside it, Figure 4.8, the absorption spectrum for a 5ppm BG compound mixed with DI water in dried lake sand, is plotted alongside the same spectrum where the pure water absorption spectrum for the same cuvette has been subtracted. The black line now only shows the absorption of BG, as the water absorption has been subtracted, making it easier to investigate the dye without implications of water. This subtracted "purer" BG spectrum, black line, is the type used in the further investigation below (except for experiment 4). Each of the cuvettes were then
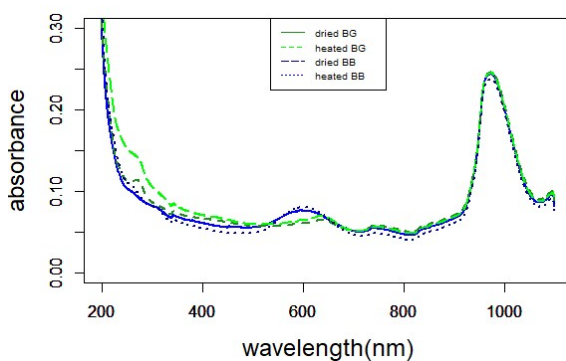
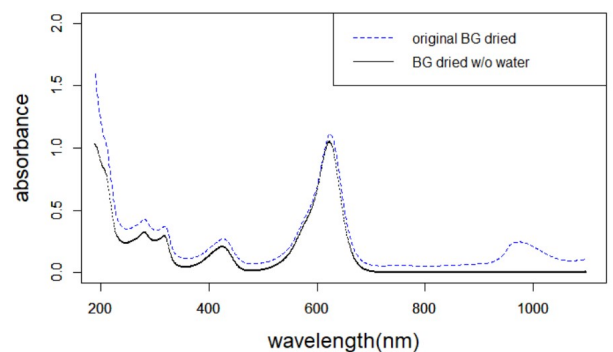

Figure 4.7: Water Absorption Spectrum for all Cuvettes

Figure 4.8: Absorption Spectrum for BG and Water

marked, so that the unique absorption noise could be removed for each of the 4 cuvettes that were used throughout the experiments.

4.3 First experiment: BB, BG, RB and PR in dried and 140°C heated lake sand with DI water

The results of PR differed from the other dyes and will be presented by itself in section 4.3.6 after the results from the other three.

4.3.1 Initial Absorbance Data of BB, BG and RB

5ppm mixtures of BB, BG and RB, all with DI water, were placed in cuvettes. One round was done with dried lake sand in the four cuvettes, and another in 140 °C heated lake sand. The same cuvette was used for the same dye but rinsed between experiments. Over the next 7 hours, the absorption spectrum was measured.

The collected data can be seen in plotted over time in Figures 4.9, 4.10 and 4.11 respectively. Keep in mind that water absorption is extracted in all data sets to minimize confusion.

In all plots, the peaks over time match the expected wavelengths well. The peak absorbance is also the highest at time zero and decreases step by step over time, with the lowest peak absorbance as the final value measured. When comparing the absorbance peak value for the same die, just with the heated and dried sand samples, they appear very similar - this indicates little change in concentrations when it comes to the two different sand treatment methods.

When comparing the changes in peak absorbance in between the dyes, BG has by far the biggest decrease over time - this indicates that BG was absorbed the most. Third aspect to note is the visible increase in the UV-range for the heat treated sand tests compared to their dried sand partners.
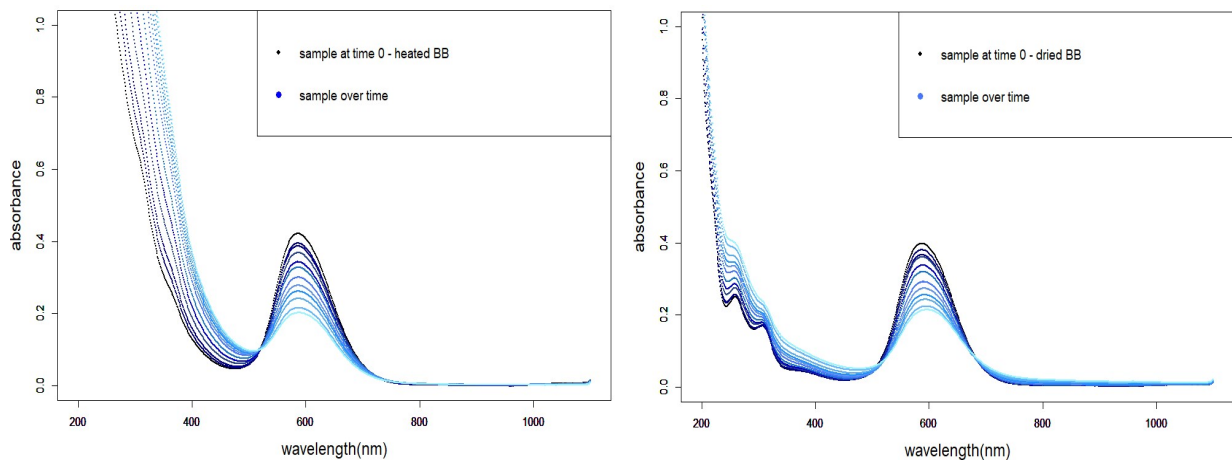

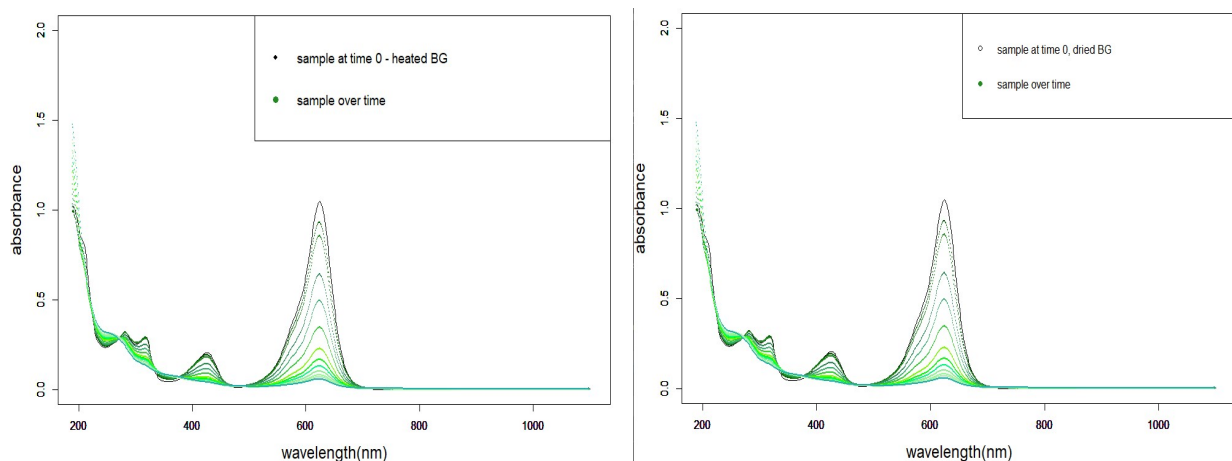Figure 4.9: Absorption Spectrum of Dried and Heated BB

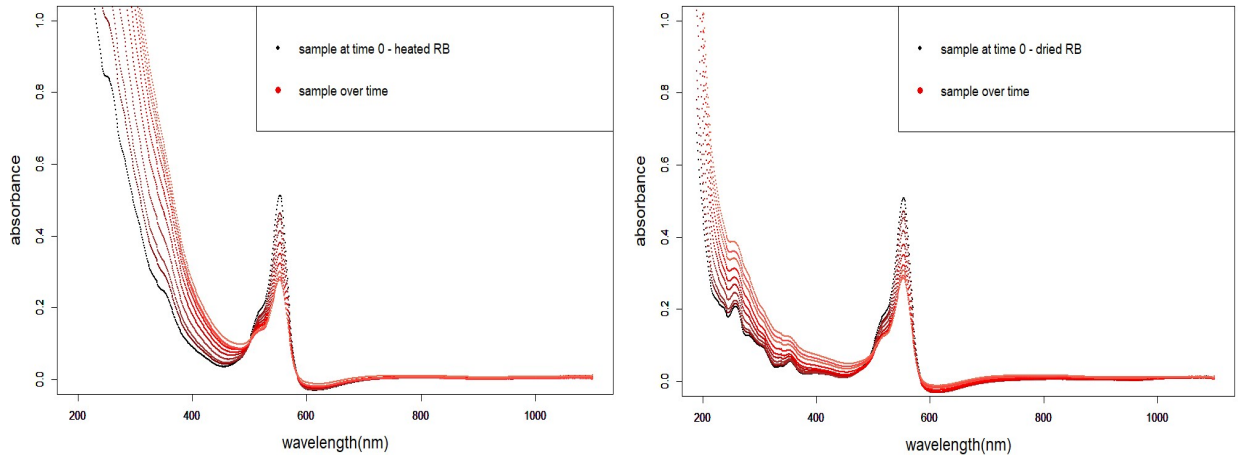Figure 4.10: Absorption Spectrum of Dried and Heated BG

Figure 4.11: Absorption Spectrum of Dried and Heated RB

4.3.2 Differences in Absorbance for Heated and Dried Samples

When comparing the decrease at peak wavelength for the cases of dried and heated sand with the same dye, their decrease seems to be very similar.
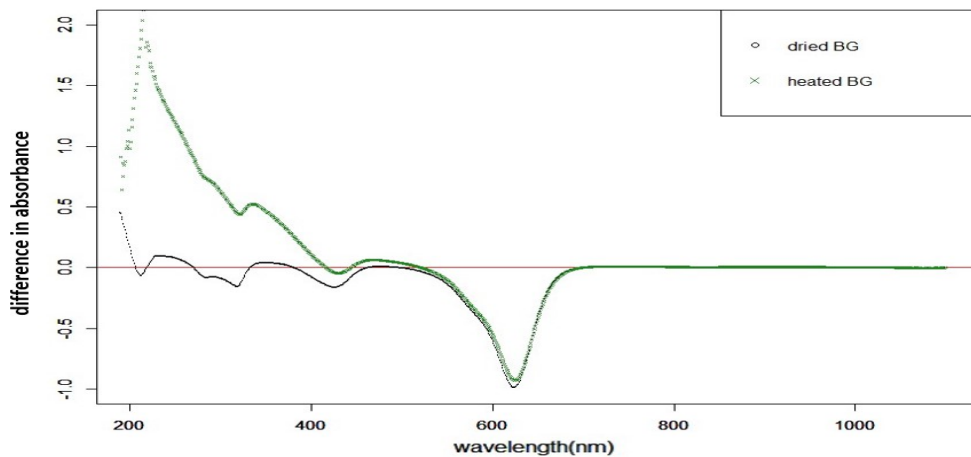

Figure 4.12: Difference in Absorbance at Start and End for BG

The biggest change from dried to heated sand is shared with all dyes; the heated sand adsorbs more over time in the UV-range. In Figure 4.12, the result of subtracting initial and final absorbance-ranges for both heat-treated and dried BG can be seen. In the Figure the negative dip at 624nm that shows the total change in concentration of BG showcases the similarity in sand absorption between the two tests. The Figure also displays how the increase in the UV range is larger for the heat-treated as the subtracted line for BG with the heated sand lies significantly above the other. This increase in UV absorbance can be explained by how the bacteria die during heat treatment and how these dead microorganisms seem to make the compound absorb more at the lower ranges. The fact that this increases over time indicate some release from the sand to the liquid. As this only happens with the heated sand, some release or new formations of new compounds in the sand must happen during the treatment.
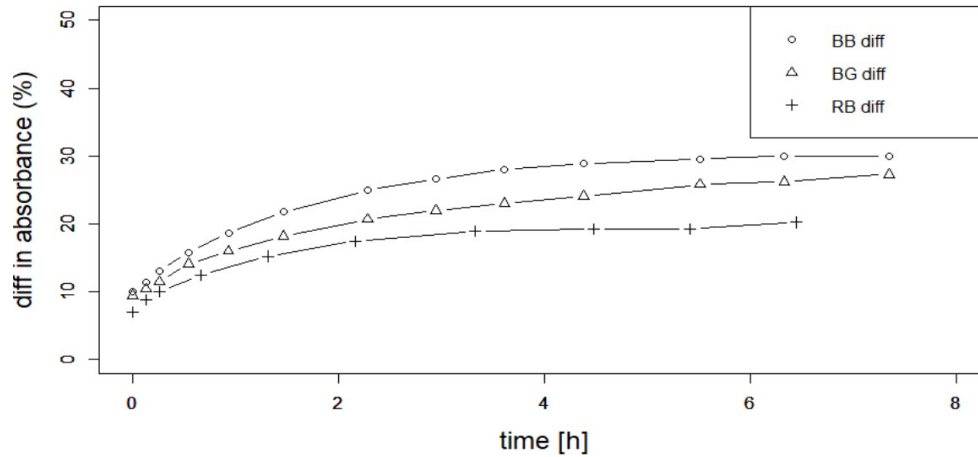
Figure 4.13: The difference in heated and dried sand absorption at 400nm for all dyes

This increase is already present at time zero, but keeps increasing as time goes, as seen in Figure 4.13. At time zero, the absorption increases about 10% for all dyes and rises towards 20-30% as time goes by. However, as the difference in absorbance at start and end only showed significant differences in the lower spectrum, this lower-wavelength difference in absorption values does not seem to affect the dyes.

4.3.3 Absorbance Peak Shifts over Time

In the Figures showing absorbance over time (Figures 4.9, 4.10 and 4.11) the peak wavelength values seem to stay more or less at the expected peak. However, when checking for the true maximum absorbance in the peak, some variations emerge; see Figure 4.14.In this Figure, the distribution of all the different measured peak absorbance values can be seen. Both RB and BG had very stable values that stay at ± 1 the expected values of 554nm and 624nm, respectively. Heat-treated BB matches the expected value, of 588nm, the least. However, as can be seen in the Figure of absorbance over time for BB heated, the peaks are relatively plateaued in this range. This plateau means that the maximum absorption value, even at 7h, is comparable to the value at the expected peak and Beer Lamberts Law still holds.
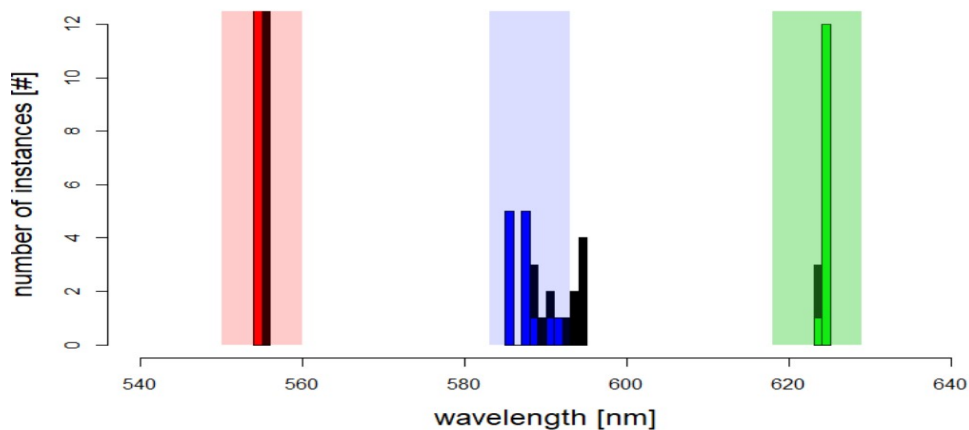

Figure 4.14: Variation of peak absorbance values over time for RB (left),BB (middle) and BG (right) in DI water. Sections covering ± 5nm of the expected value are visualized in the correlated colour. The values with dried sand are shown in color bars and the corresponding $140°$C heated sand values, in black bars.

4.3.4 From Absorbance over Wavelength to Concentration over Time

Using the peak absorbance values together with Beer Lamberts law, Equation 2.1, the concentration can be calculated. The length and extinction coefficient from Table 2.2 are also needed for the calculation. As peak absorbance has been found to be stable at the expected values, the extinction coefficient stays the same even as the concentration decreases. For the initial concentration for dried BG the computation becomes:

$$C_i = \frac{A}{l[cm] \cdot \varepsilon[L/(cm \cdot mol)]} = \frac{1.110057}{1.00 \cdot 130000} = 8.5389 \cdot 10^{-3}[mol/(m^3)]$$
$$ppm_i = C_i \cdot M[g/mol] \cdot 1000[m^3/kg] = 8.5389 \cdot 10^{-3} \cdot 475.6 \cdot 1000 = 4.06\text{ppm}$$

Notice the conversion calculation from concentration to ppm that includes the molar mass (listed in same table as extinction coefficients).

The initial/final concentrations for all six tests with DI water was calculated to be as in the list below.

	initial	final		initial	final
BG dried	4.06	0.44	BG heated	4.05	0.65
BB dried	3.61	2.05	BB heated	3.75	1.87
RB dried	4.34	2.66	RB heated	4.37	2.60

Table 4.1: Overview of Initial and Final Concentrations of the Dyes

All values of concentration over time calculated with Beer Lamberts Law can be seen in Figure 4.15. Already when looking at the absorbance over wavelength plots, two trends could be seen: an indication of a small change between heat-treated and dried sand for the individual dye, and a bigger overall absorbance for BG. These indications are supported further here as the concentration falls from 4ppm to well below 1ppm, with the most significant amount of the absorption happening the first 2 hours, especially when looking at the curve for BG. More on this later.
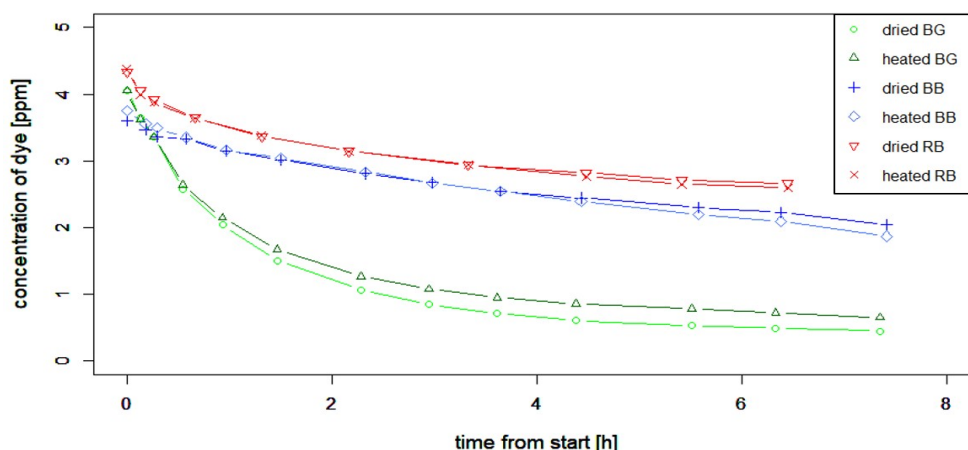

Figure 4.15: Concentration of Dyes Over Time

4.3.5 Percentage Absorbed Over Time

Figure 4.16 shows the same data just converted into percentage over time for simplicity; this is also called the adsorption coefficients. See equation 2.2 for the calculation method.

This calculation method will continue to be the way the percentage over time data is calculated throughout the paper. The final amounts absorbed for each test, after the 7h, is listed in table 4.2. All absorption values calculated are visible in Figure 4.16, similar trends to before when it was concentration plotted, but now opposite. As was obvious in
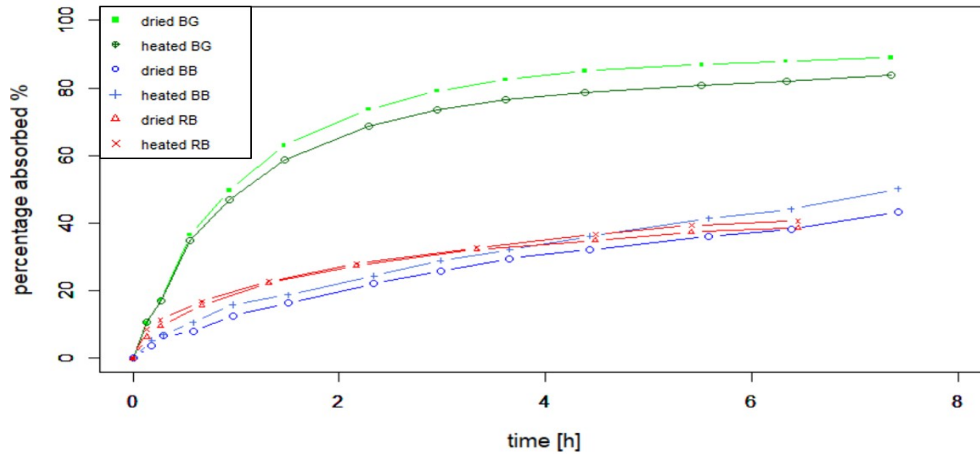

Figure 4.16: Percentage of Dye Absorbed Over Time

the concentration plot too, the dried and heat-treated sand values for the same dye are very similar in the amount being absorbed over time - but not identical. When investigating an individual dye and the difference in heated and dried sand, there is a tendency of either the dried or the heated treatment being the most efficient at absorbing. For example, BG absorbs better with the dried sand than with the heated sand. However, as it varies between the dyes which of the dried and heated sand absorbs the best, no overall general trend between the dried and the heated can be made.

	conc.	fin. slope		conc.	fin. slope
BG dried	89%	1.01	BG heated	84%	1.72
BB dried	43%	4.49	BB heated	50%	5.83
RB dried	48%	1.08	RB heated	49%	1.03

Table 4.2: Final Concentrations of Dyes in DI water

BG, with both dried and heated sand, has the highest rate of absorbance happening the first 2h and then starts to flatten out. The significant amounts of absorbance happening the first 2 hours are unique to this dye, as the other two show slow and steady absorbance at the beginning. Around the midway point, RB, both dried and heated, seems to flatten out similarly to BG. RB takes longer to flatten but does in a similar way reach a low slope-value where there is only a small increase in absorbance as time passes. When looking at this in a chemical sense, one would say that it seems like the solution has reached an equilibrium. The BB, both dried and heated, is different in terms of equilibrium reaching. Here, the slope varies less over time, and as the slope hasn't started to decrease, this indicates that more dye could be absorbed if the experiment had lasted longer. When investigating the change in slope between the last two time measurements, BG's and RB's slope give a slope that correlates to 1% more absorbance per hour whereas the BB's give around a 5% increase per hour as displayed in table 4.2.

4.3.6 The Result of PR

It has been mentioned earlier that PR is often used as a pH indicator. The absorbance qualities of PR is connected to both its colour and pH. It looks yellow at lower pH values (around 6.8), values under seven are referenced as acidic. PR under these conditions have a maximum absorbance at 443 nm. If the pH increases up to 8.2 (weakly alkaline), the maximum absorbance lies around 570 nm and PR turns more red [10].

PR was tested alongside the other three dyes in the same way. Originally, it was, as with the other dyes, meant to look at the absorbance of PR over time in regards to the sand. But, as PR has this ability to change the maximum wavelength of absorption, the situation becomes more complex. How can one use the decrease in absorbance at one specific wavelength as an indicator of sand filtration, when the case might be that the maximum absorbance peak is simply being shifted?

The initial and final absorption spectrum for PR can be seen in Figure 4.17 below. Especially when looking at the dried samples absorbance values at the black (initial) and red (final) peaks, the idea that concentration might not be going down is supported. When investigating the initial and final peak, at absorbance values 0.18 and 0.22, it might seem like concentration is going up - as concentration is directly proportional to absorbance when following Beer-Lambert. Of course, the concentration of the dye cannot increase in a closed test environment like this was undergone in, but any significant filtration of PR by the lake sand is not present. There is however, something to say about the pH -
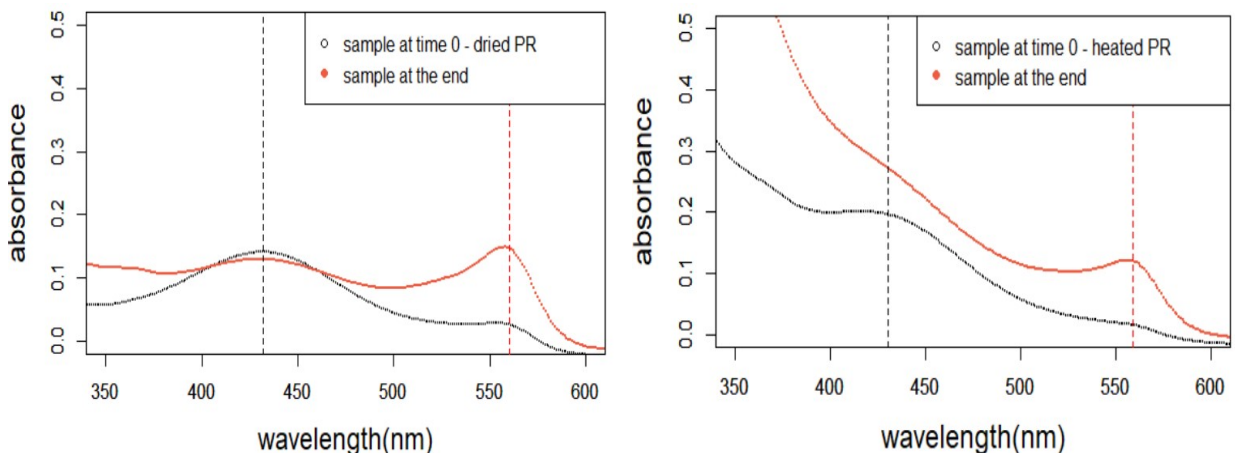

Figure 4.17: Initial and Final Absorption Spectrum of Dried and Heated PR

this is after all what PR is normally used for. Although it's not completely clear, it can be said that the initial peak lies at a wavelength at 432nm and the final peak around 560nm. Following literature this indicates a shift in pH from weakly acidic to weakly basic [16]. As the pH in water by Danish law should be between 7,0 – 8,5 with regards to quality and the water supply system [13] - PR proves itself useful after all.

4.4 Second experiment: MB in dried, 140°C and 500°C lake sand with DI water

To gain some further insight in how temperature affects absorbance, Methylene B was tested with three different temperature treated lake sand samples - the room temperature dried, the 140°C and a new 500°C sample. The previous tests have shown no true trend in how the temperature affected absorbance. But maybe this will?

As before the three samples were mixed in a roughly 5ppm concentration of DI water, placed in a cuvette with Avnsø lake sand and sampled regularly in the spectrophotometer
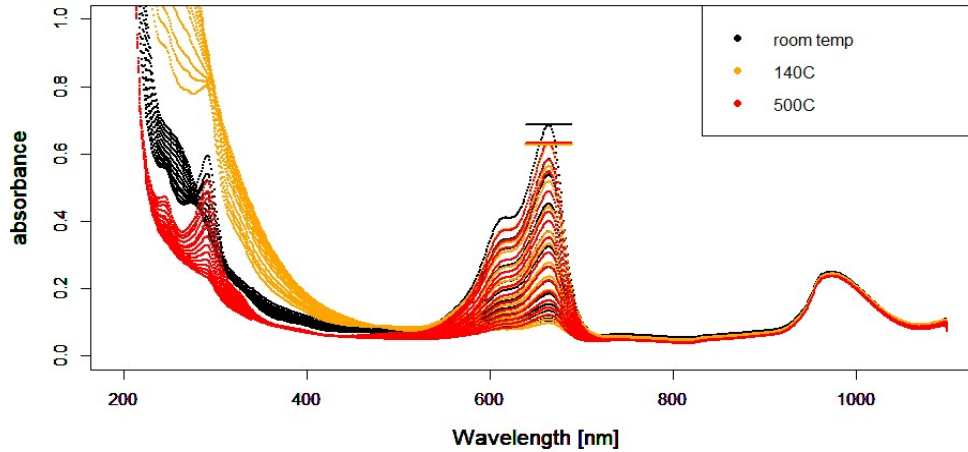
Figure 4.18: Methyl B Absorbance Across Different Sand Treatment Temperatures

for approximately 7h.

The raw spectrophotometer data can be inspected in Figure 4.18 (water adsorption is not removed). Similar trends in the difference of room temperature dried and 140C dried can be seen as with BG, BB and RB before - the UV range absorbance increases as an only significant difference. Interestingly enough, the same range experiences a decrease with the 500C data. Some of the particles that exist, or are active components, in the 140C sample and increases absorption values in the UV range are in other words gone, or are at least no longer absorbing, after being dried in 500C.

For the peak at 664nm that responds to the MB concentration, the sample's behaviour is comparable across all three data sets. So like before, there might be a big difference in the UV-range, but this difference in absorbance values over time does still not seem to affect the adsorption of the industrial dye. Something to notice, however, is that the room temperature tests seem to start at a higher concentration than the other two.

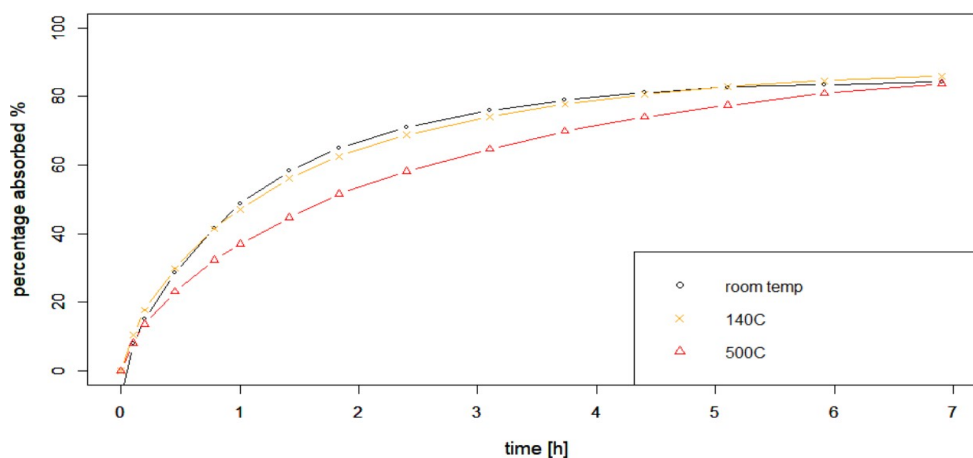Continuing, the percentage over time was looked into, see Figure 4.19. In this Figure, the

Figure 4.19: Percentage Absorbed Across Different Sand Treatment Temperatures

500C sample is significantly less adsorbed during the experiment when comparing it to the other two, who have a solid positive correlation of 0.99 for the percentage adsorbed

over time. However, all three end up with very similar values of final adsorption (see table 4.3). The final slope of the 500C sample is also significantly higher, indicating that the adsorption of this sample might surpass the other two if the experiment had lasted longer.

	conc.	fin. slope
room temp	84%	1.05
140C	85%	1.41
500C	83%	2.98

Table 4.3: Final Concentrations of MB at Different Temperatures

4.5   Third experiment: BB and BG in Sea Water

The same experiment as earlier, was now taken on with a twist. BB and BG were still used with the dried and heated Avnsø lake sand, but instead of mixing the dyes with DI water from the lab, seawater was used to see how the difference could affect absorbance results. The saltwater differs in pH and has microorganisms and roughly 3% salt (NaCl), so one might expect an increase in absorbance due to the ion conductors and living microorganisms.

Similarly to the previous test, the absorbance values across wavelengths were used to get the final percentages of absorbance versus time. In Figure 4.20 this new seawater data is compared to the previous measurements with the DI water. The data set matches
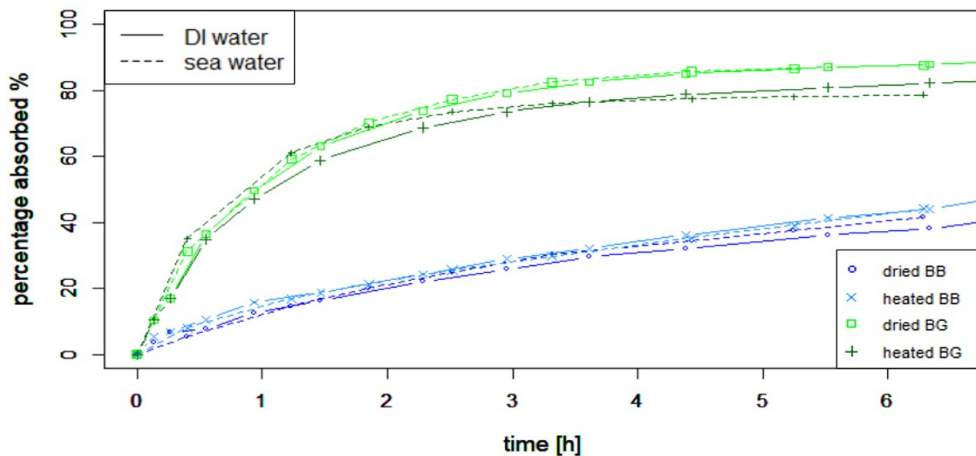

Figure 4.20: Percentage of Absorbance in DI and Sea Water Over Time

very well with the previous and shows a clear trend that changing from DI water to seawater does not affect absorbance in any significant way - the microorganisms, salt and pH showed to be irrelevant in this case. As two separate experiments show such similar results, this builds a stronger case in regards to the lack of overall trend in absorbance between the dried and heated sand treatment samples. To further investigate the similarities between the two tests, the correlation was calculated with the Equation 2.3. To make it as precise as possible the time reference of each sample, in terms of hours into the experiment, should be the same. Linearity was assumed between each time data collection was done to compare the samples at the same time-stamps. As the base experiment has the most data collected, 13 times versus the nine times, the base experiment data was modified to match the time-stamps of the seawater data. The correlation for each of
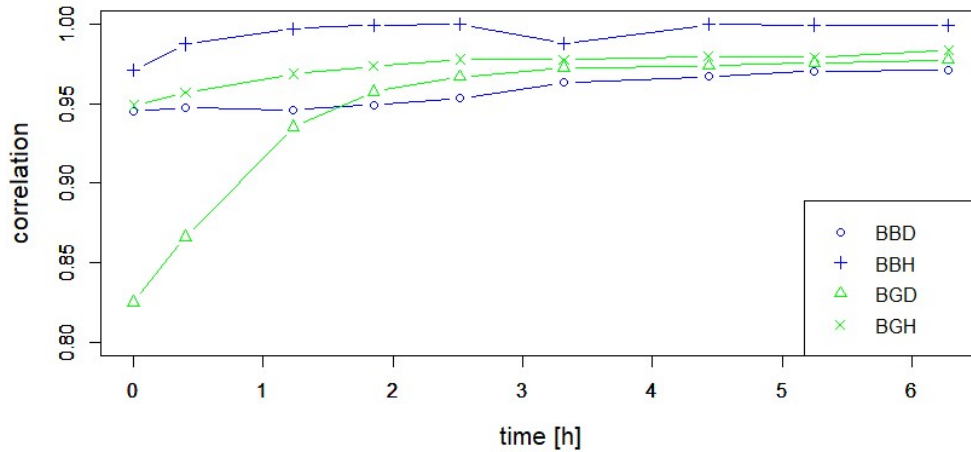
Figure 4.21: Correlation between DI water and Sea Water Data

the dried and heated data sets can be seen in Figure 4.21. Across all data sets, even with the lowest correlation value of 0.83 at time zero for dried BG, all samples show an evident trend of positive correlation. The strong correlation indicates little difference in the samples that have been compared.

4.6 Fourth experiment: BB and BG in Sea Sand

A very similar comparison-experiment was underdone with the same initial conditions as the base experiment, only this time, the Avnsø lake sand was replaced with sea sand from the Roskilde fjord.

The resulting absorbance percentage over time can be seen in Figure 4.22. Especially for BB, this new sea sand data seem to lie above the old throughout the entire experiment, meaning absorbance is higher as a stable trend. The data for BG is closer to the old, and it is difficult to say anything for certain with this Figure.

Calculating the difference on average, by taking the mean difference in the samples over
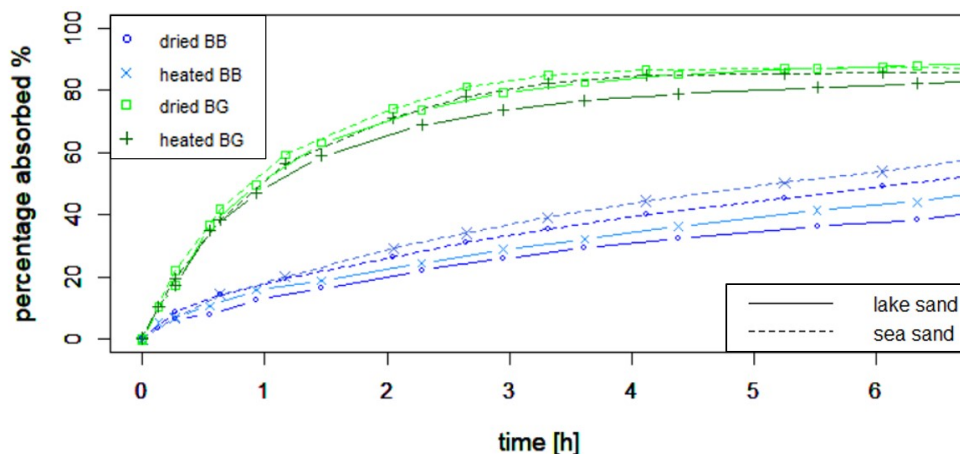

Figure 4.22: Percentage of Absorbance Over Time in Sea Sand

time, there is an 6% and 7% increase in absorbance for BB heated and dried, respectively. BG shows the same tendencies, but weaker; a 3% increase for the heated and a 1% increase for the dried sample.

The final percentage absorbed gives further insight, and the values are listed in table 4.4.

As expected, the final values for BB show a considerable increase in both the dried and the heated samples. For the heated BG sample, the same tendency is present, but for the dried BG samples, the opposite is true - here the lake sand absorbs 2% more than the sea sand.

A percentage over time plot can be used to explain how the average difference for the

	lake sand	sea sand		lake sand	sea sand
BG dried	89%	87%	BG heated	84%	86%
BB dried	43%	54%	BB heated	50%	60%

Table 4.4: Final Percentages Absorbed in Lake and Sea Sand Samples

dried BG sample can be positive 1% while the final value is negative 1%. Assuming linearity between each data collection point, as before calculating the correlation, now gives the possibility to compare the percentage absorbed over time for each test and the result can be seen in Figure 4.23. As before, BB shows an apparent trend of always increasing. BG is a more unstable. For BG heated, even though there are times where the difference is negative, meaning that lake sand had a higher absorbance at this point, the majority of points have the sea sand coming out on top, which includes the final measurement as it is above the red zero-line. The final difference for BG dried, however, is negative, indicating the fact that the previous test had a higher final percentage absorbed. But, as the BG heated sample, the majority of data points still lie above - meaning that for most individual instances, the sea sand absorption at the time was higher.
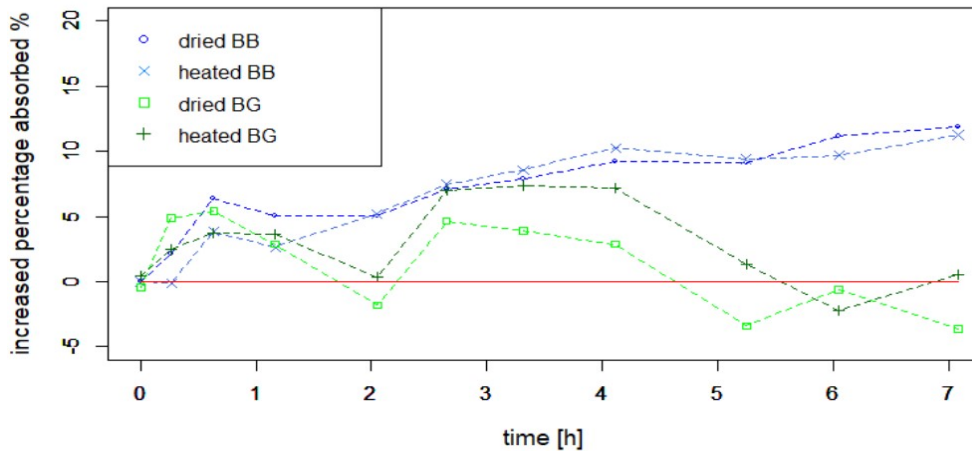

Figure 4.23: Increased Percentage of Absorbance Over Time in Sea Sand

5 Discussion

Before starting on the main discussion regarding the results just discussed, some uncertainties regarding those results will be discussed.

5.1 Investigating Uncertainties in Results

In any research, there are uncertainties, and these are important to address to ensure validity. In this project all data come from prior experiments done by the supervisor and were made only to plan the upcoming project. But as COVID-19 prevented any new data collection, this test data was used. COVID-19 lockdown also prevented any replication of experiments to decrease uncertainties in findings.

The uncertainties that will be investigated further on are ones related to data collection from the instruments, solution homogeneity over time and the initial solution mixture.

5.1.1 Uncertainty in Spectrophotometer Data

The absorbance data from 800 to 1100nm was used to test the uncertainties in the data from the spectrophotometer. As the dyes are not absorbed in this range, absorbance values should be non-existent (when disregarding the water absorbance). By making a histogram from 52 runs over the 300-wavelengths measures, the histogram placed to the left in Figure 5.1 was made. A standard deviation of 0.00436728 absorbance was calculated across the entire data set, and seen in terms of concentration for BG and BB (using Beer Lambert's law) this correlates to 0.033ppm for BB and 0.016ppm for BG. Even though this deviation is based on data from 800 to 1100nm, it is assumed to hold for the entire range as the spectrophotometer is assumed to be stable in its measurement accuracy. The figure on the right shows this deviation plotted as black error bars from a point for concentration for BG. The standard deviation is so small it does not cross the line of the circle displaying the point. It has therefore been decided to look away from any uncertainties when regarding the spectrophotometer data.
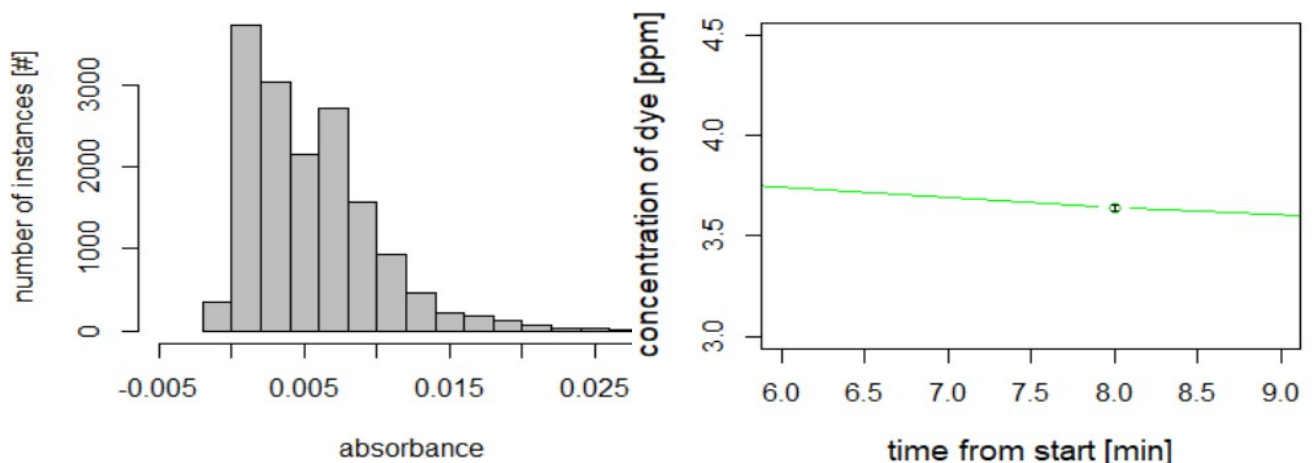

Figure 5.1: Uncertainties in Spectrophotometer Data

5.1.2 Uncertainty in Dye Distribution Over Time

Only a cuvette of 1x1cm was filled with the solution to measure absorbance in the spectrophotometer. When using that data as a measurement of absorbance, it is assumed that

the fragment of the solution tested is a good indicator for the entire cuvette. An important possible uncertainty here would be created if the dye did start sinking in the container from where the cuvette was filled. If that happened, whatever concentration the spectrophotometer data indicated, would only be telling something about the concentration in that layer.

> **A Derivative of Brilliant Blue - E133**
>
> [H] The BB mainly worked with in this paper is the Brilliant Blue G or Coomassie Brilliant Blue and is not commonly used in food. However, there exist many versions of derivatives of BB. One of them is Brilliant Blue FCF and is also known as E133. E133 is one of the most common blue food dyes in Europe, e.g. it's what makes the blue m&m and IceStorm Powerade blue [26]. E133 is also the main dye ingredient in many blue food colouring products. It has also been determined that some specific population groups, mainly toddlers and children, have a moderate risk of consuming too much of this E-substance in a study done by The European Food Safety Authority (EFSA) [26].

Figure 5.2: Jars of E133 of Different Concentrations After 6 Days

A test was done with E133, which is comparable to Brilliant Blue FCF, to see whether or not sinking of the dye occurred. Different concentrations were made for testing with normal danish tap water. Unfortunately, a concentration of 5ppm of E133 turned out to be too weak for the naked eye to spot the colour, so stronger concentrations were used. In Figure 5.2, the different concentrations can be seen after six days of standing still in room temperature. As none of the dyes showed any sign of sinking, this uncertainty was also discarded.

5.1.3   Discussion on Uncertainties at Initial Concentration

The initial concentration was supposed to be 5ppm, but all calculated values are found to be lower, which raised an unforeseen question of uncertainties.

There are several possible explanations for this. As the dyes were in a powder form, any possible humidity would make it heavier such that concentration relative to weight would be less than stated on the package. Also, the plastic bottles where the solutions were kept got stained, meaning some dye got stuck inside. Both phenomena would decrease the actual concentration at the start, which makes the calculated values acceptable.

5.2   Discussion on Results

Color agent absorption was observed in all conducted experiments. Overall, across all experiments, the lowest amount of dye absorption was 43%, and the highest 89%, after 7h. The form of absorption over time had, in general, two forms: BB and RB showed a close to linear absorption over time, whereas BG and MB absorbed faster the two first hours and then flattened out. It was also BG and MB that reached the absorption values of over 80%, whereas the other two stayed between 40-50%. This value does not necessarily mean BG and MB are absorbed better, only faster. When analysing the final slope, BB had a five times steeper slope than BG, meaning that if the experiments were run over a longer period, BB might have surpassed BG in terms of absorption - as the latter showed signs of having reached equilibrium. Continuing, the discussion of results will focus on the three hypotheses. In Table 5.1, the relationship between hypothesis, experiment number and their results are displayed.

Hypothesis	Experiment	Relevant Results
A	1,2,3,4	Figure 4.9-4.13,4.16,4.19,4.20,4.22. Table 4.1-4.4
B	3	Figure 4.20,4.21
C	4	Figure 4.22,4.23. Table 4.4

Table 5.1: Overview of Link Between Hypotheses, Experiments and Results

A. Heat treatment of sand will not affect adsorbing abilities within the tested range.
All experiments conducted included different sand treatments to inform hypothesis A. The major tendencies in the dried and 140°C heated sand samples also stayed constant across all tests. In total, the difference in absorbance between the two treatment methods was less than 5%.

Heat treatment of the sand was primarily tested as it can be a way to recycle the sand after use as the dye recomposes at high temperatures, making the sand ready for new adsorption. The most significant tendency difference for the 140°C heated sand samples, compared to the room temperature dried sand, was the increase in absorption in the UV range. This increase could be a result of dead microorganisms that get mixed in the solution, causing added absorption at specific wavelengths. It could be interesting to further investigate by observing the differences in the sand before and after heat treatment. Still, as the heat treatment barely affects dye absorption, it does not need to be a priority.

When including the test with 500°C treated sand, the picture becomes even more evident. The particles that were killed and released at 140°C, increasing absorption in the UV range, are no longer there. They seem to be gone, or burned, as absorption in the UV range is decreased to below original levels. This UV-range absorption still doesn't affect dye absorption, so the idea that the sand can be heat treated as a way to decompose the dyes and make the sand ready for new absorption is supported.

There were both instances of the dried and the heated sand samples adsorbing the most. For the dyes that were tested under the three different scenarios; DI water with lake sand, DI water with sea sand and seawater with lake sand, it did, however, stay constant which of the dried and heated sand samples adsorbed better. For BB, the heat-treated sand test had higher adsorption, and for BG, the dried sand test. Why this difference emerges could be looked into by testing the sand samples, before and after adsorption, with the SEM.

Based on all results, it is highly likely that the hypothesis is true, and heat treatment is

suitable as a way to decompose the dye and recycle the sand.

B.The sand will show similar purification properties when used in seawater and demineralised water

Experiment 3 was conducted to test this hypothesis. Seawater proved to give the same results as DI water when tested with BB and BG solutions in lake sand. The mean correlation across the four different tests, one with dried and 140°C heated sand samples for both BB and BG, was 0.97 - which is a strong positive correlation. This correlation indicates that the results found on absorption can be extrapolated to include cleaning of coastal regions which increases the application potentials. The findings support the second hypothesis.

C.Sea sand has better adsorbing abilities than lake sand

Experiment 4 was conducted to inform this hypothesis, showing that sea sand increased BG and BB absorption. The mean increase for all cases, with both dried and 140°C was a little more than 4% when compared to the tests with lake sand. The investigations of the elemental and mineral analysis with x-ray diffraction and SEM showed similar compounds and phases. Both sand samples were found to consist mainly of silicate, but other minerals like iron, titanium, calcium, potassium and sodium were also found in both samples in different amounts. Especially for titanium and iron, which was more present in the lake sand sample, the adsorption abilities are known to be good. But, the sea sand showed higher adsorption abilities in these tests. SEM pictures revealed the sea sand to be more uniform, and as uniformity is one of the main factors when it comes to efficient sand filtration, as mentioned in section 2.3, this could explain the adsorption increase. Regardless, the findings also support the third hypothesis.

5.3   Photocatalysis Study Comparison

The study discussed in this section is part of the same project of water treatment by this thesis' supervisor [15].

Photocatalysis is an emerging technology that also has great potential in cleaning polluted water. A study that looked at how a variety of industrial dyes can be discoloured by photocatalysis using Mg-doped thin films and sunlight to irradiate the water will be discussed here. Most studies on photocatalysis stir or recirculate the water, but this study was done with static water; similar to the method used here. Specifically, the study also looked at the difference when using DI-water and seawater with seven different dyes; 4 of which that match the ones tested for sand adsorption in this project. Similar to the sand adsorption test; Brilliant Blue and Green had similar, or slightly better results with seawater when compared with DI-water. Methylene Blue and Rhodamine B were worse.

This new information makes it even more pressing to test more of the dyes in seawater to see if the trend for photocatalysis is the same as with sand adsorption, before a conclusion on this factor can be made.

6 Relevance for Commercial Water Purification in Scandinavia

To further add to the discussion, some insights given by water treatment professionals in Norway and Denmark addresses the relevance of the findings for the water treatment industries in these countries. Ultimately, the set-up used in this project was scaled up to compare it to industrial water treatment plants.

6.1 Relevance for Norwegian and Danish Water Industry

Both Norway and Denmark use sand filters in water treatment, but as the two countries have different topography, soil and population density, the areas of application vary.

In Norway, the overall treatment level of wastewater is 92% [20], but only 10% of facilities include sand filters. Most wastewater cleaning facilities use advanced chemical and/or biological methods; the rest use more straightforward mechanical methods that only remove the biggest particles. The advanced treatment facilities tend to be situated in the south-east of the country, regions Vest-Agder to Østfold, as the wastewater there drains to the North Sea. All states draining wastewater to the North Sea have declared regulation agreement regarding the amounts of phosphorus and nitrogen, typical pollutants from human urine, detergents and manure.

The situation is similar in Denmark. A total 95% of all wastewater is treated – and often to a higher standard than the legal requirements [44], but the standard cleaning method does not include sand filters. Over 90% of all wastewater is treated at the 200 to 300 biggest and most advanced facilities that use the conventional method - without sand filters. Some of the smaller wastewater facilities might still be using sand filters, as in Norway, but no specific data on this has been found. It is however known that there are about one third the amount of wastewater treatment facilities in Denmark when compared to Norway ([25],[31]). As only the smaller facilities still use sand filters, there are likely fewer in Denmark.

The relevance of sand filters is bigger in the water supply industry for both countries.

In a conversation with Trond Lohne, the CEO of Vannplan; a company that help drift and ensure the quality of water supply in Norway, he identifies the uses of sand filtration in the Norwegian water supply. The most typical way to treat the water, he says, is chemical precipitation for flocculation, which is removed using a sand filter and then UV radiated. The sand filter is in this case used as a material to stop the precipitated matter and therefore needs to be back-washed regularly. A problem here though is that as the water treatment facilities both are many and small (to avoid expensive pumps to distribute over mountains), they are often run by locals with close to no education on water treatment - and sand filters need regular maintenance.

Natural sand filters are also used in Norway in simple drainage wells. These wells are used for extraction of inflow of surface water and clean the water through different sand layers. These sand layers create a filter similar to the gravitational filters presented in the first chapter. The negative aspect of these drainage wells from the Norwegian aspect is that they often need to be dug in the valleys, which makes pumps necessary. Whereas Norwegians have the luxury to mainly use surface water from sources far away

Figure 6.1: A Sand Filter in Operation in Denmark [42]

from human activities where gravitational energy can be used to distribute it, Danes live in a flat and populated country. In Denmark, the water supply therefore depends on wells reaching the groundwater 50-150 meters below ground. Groundwater has already gone through the natural sand layers in the ground, but is still in need of additional treatment. The usual danish treatment for water is oxidation, to remove methane and hydrogen sulphide, followed to sand filtration to remove iron and manganese [42]. Figure 6.1 shows an example of sand filter used in Denmark.

Groundwater, even though it is naturally filtrated, still have some prominent sources of pollution. Typically one would believe that this was more of an issue with surface water as it is an open-air source. But the most significant contamination source is usually animals as the water sources lie up in the mountains far from humans and industry (T. Lohne, personal communication, May 12, 2020). In Denmark, measures have been taken to reduce pollution in the water reaching the treatment facilities. One is the decentralisation of the water drills that supply the groundwater to the treatment facilities.

Jesper Furdal, the CEO of Awell - a Copenhagen based well drilling company - states that the most prominent sources of contamination in the groundwater are decomposition products from pesticides and chlorinating solvents from the industry. He continues to say that another problem is that as the Danish population grows, older drillings that were created far away from industry and neighbourhoods get closer and risk pollution. In these cases, the closing of the well is typical. But other solutions do exist, like in Bagsværd, a suburb of Greater Copenhagen. Here several shallow wells were built do pump contaminated water out, keeping the groundwater drinking source below clean.

6.2   Upscale Scenario

The filtration looked at in this project consist of 40mL contaminated water in a 35 cm^2 cuvette with 2mm of sand; in other words, very small compared to real-life facilities. For example, the two wastewater treatment plants that handle the Copenhagen Area take 350 000 and 750 000 population equivalent every day [31]. One population equivalent produces on average 200 L a day [36].

If the data from the DI water and dried lake sand with BG is investigated, it takes approximately 3.5 hours to remove 80% of the dye. Assuming this is an appropriate amount of

removal, the flow rate can be calculated in this way [17];

$$\text{flow rate} = \frac{40\text{mL}}{35\text{cm}^2 \cdot 3.5\text{h}} = 0.0032\text{m/h}$$

Normally, flow rates of sand filters are recorded to be around 0.1-0.3 m/h, making this estimate very low in comparison - 2 orders of magnitude smaller. That being said, as the contaminated water only lay on top of the sand layers and the commercial filters would have the water running through which increases the surface area of contact, the value found here is a minimum compared to what could be expected if the water flowed through. On the other hand, it is also assumed that an 80% removal is efficient enough (which it normally isn't) and that the system can be linearly scaled up which makes the comparison uneven in the other direction.

Using an online tool called map developers, an approximation of a chosen area can be made. This tool estimates Avnsø lake to have an area of approximately 44982 m^2. With the recorded max depth of 8m [43] an approximation of volume is made with the assumption that average depth is half of maximum depth. Sand density is approximated to be 1.63 kg/L [11]. The 2mm of sand in the container of 35cm^2 corresponds to 7mL of sand.

$$\text{Cleaning rate} \quad = \quad \frac{40\text{mL of Water}}{3.5\text{h} \cdot 7\text{mL of Sand} \cdot 1.63\text{kg/L}} = 1.00\text{L/(kg h)}$$
$$\text{Avnsø Volume} \quad = \quad 44982 \cdot 4 = 179928\text{L}$$

The volume of Avnsø corresponds to 900 PE, which is 0.25% the capacity of the smaller Copenhagen area treatment plant Damshusåen [31]. If all of Avnsø was to be cleaned of 80% of BG in a day the amount of sand needed would then be:

$$\text{Sand Needed} = \frac{\text{Avnsø Volume}}{\text{Cleaning Rate} \cdot 24\text{h}} = 7489\text{kg}$$

If these 7489kg were to be laid as 2mm - as in the experiment, an area of 2295m^2 would be needed. An area comparable to two Olympic standard swimming pools (that each are 50x25m), or of course, it corresponds to about 3% of Avnsø lake surface. But of course, scaling this up to the size of Damshusåen instead, would give an area 400 times this, making the set-up in this project quite unhandy.

7 Conclusion

Three main aspects regarding the use of sand for water filtration has been examined. Both the Avnsø lake and Roskilde fjord sand samples filtrate water solutions contaminated with five different industrial dyes that have been tested in this project. The industrial dyes are used as models of pollutants. Both sand samples adsorbed Brilliant Green and Methylene B the most, reaching over 80% adsorption.

The first main aspect investigated was heat treatment of the sand samples. Heat treatment, both at $140°C$ and $500°C$, affect sand adsorption abilities only to a small degree when compared to sand dried at room temperature. Heat-treatment could therefore potentially be used as a way to recycle the sand. Overall, heat-treatment gave promising results as a recycling method, but at lower heat-treatment temperatures ($140°C$) the dye may not be burned away completely. This was qualitatively seen as increased absorption in the UV-range, and could affect water filtration efficiency long-term. Further testing should be done to investigate the minimum heat-treatment temperature.

Testing was also done with seawater to investigate effect on adsorption compared to demineralised (DI) water. The seawater was tested with Brilliant Blue and Brilliant Green, and the results were strongly correlated to the identical tests with DI-water. This correlation indicates that the sand filter can be used to filtrate coastal waters as well as freshwater. However, the seawater was not tested with any of the other dyes, and comparable research with photocatalysis found that even though the seawater did not affect the absorption of Brilliant Blue and Green - this was not the case for dyes like Rhodamine B. Further testing should be done to clarify whether extrapolation is possible. The findings in this project were therefore diverging from similar results when it comes to seawater's effect on sand adsorption.

The last aspect regarded if sand from sea and lake origin adsorbed differently. Results showed that sea sand adsorbs better than lake sand. The higher uniformity seen in sea sand as visualized with scanning electron microscopy is a likely reason for this difference, but more specific tests on uniformity should be done to verify this.

Sand filters remain relevant for water treatment today both in Denmark and Norway - mostly in the water supply chain, but to some extent also in wastewater treatment. Therefore the findings of this project are relevant for industrial applications. The set-up used here is not as efficient as the industrial ones in commercial use today, but to make a further improved comparison the contaminated water should run through the sand.

This thesis takes a firm step ahead on the possible application areas for sand filters as a method for water filtration. The application areas include the potential removal of emerging pollutants. Although further testing, as suggested here, appears relevant, gravitational sand filters remain a promising method for water purification.

Bibliography

[1] In: (2015). ISSN: 2095-6339. DOI: 10.1016/j.iswcr.2015.03.002. URL: http://www.sciencedirect.com/science/article/pii/S2095633915000039 (cit. on p. 1).

[2] Hassan Agiwaan. "Thesis: Thermal Stability of cubic and nanocrystalline arc evaporated TiCrAlN coatings". PhD thesis. Feb. 2014 (cit. on p. 8).

[3] Canada Department of Agriculture. *Glossary of Terms in Soil Science*. 1976. URL: http://sis.agr.gc.ca/cansis/publications/manuals/1976-glossary/pub1459_report.pdf (cit. on p. 3).

[4] National Center for Biotechnology Information. *Methylene blue*. URL: https://pubchem.ncbi.nlm.nih.gov/compound/Methylene-blue (visited on 05/22/2020) (cit. on p. 6).

[5] Cambridge.University. *The Scanning Electron Microscope*. URL: https://www.eng-atoms.msm.cam.ac.uk/RoyalSocDemos/SEM2 (cit. on p. 9).

[6] Corporate Finance Institute CFI. *What is a Correlation?* URL: https://corporatefinanceinstitute.com/resources/knowledge/finance/correlation/ (visited on 05/21/2020) (cit. on p. 10).

[7] P.A. Clark et al. "Slow-sand water filter: Design, implementation, accessibility and sustainability in developing countries". In: (2012). URL: https://doi:10.12659/msm.883200 (cit. on pp. 2, 4).

[8] Conservation and Art Materials Encyclopedia Online. URL: http://cameo.mfa.org/wiki/Main_Page (visited on 05/22/2020) (cit. on p. 5).

[9] D.Nabi, I.Aslam, and I.A.Qazi. "Evaluation of the adsorption potential of titanium dioxide nanoparticles for arsenic removal". In: *Journal of Environmental Sciences* 21.3 (2009), pp. 402–408. ISSN: 1001-0742. DOI: https://doi.org/10.1016/S1001-0742(08)62283-4. URL: http://www.sciencedirect.com/science/article/pii/S1001074208622834 (cit. on p. 14).

[10] G. Davies. *Phenol Red - pH indicator*. Apr. 1, 2020. URL: https://cran.r-project.org/web/packages/colorSpec/vignettes/phenolred.html (visited on 05/26/2020) (cit. on p. 21).

[11] *density of sand (dry,material)*. URL: https://www.aqua-calc.com/page/density-table/substance/sand-coma-and-blank-dry (visited on 05/29/2020) (cit. on p. 32).

[12] Edinburgh.Instruments. *The Beer Lambert Law*. URL: https://www.edinst.com/blog/the-beer-lambert-law/ (visited on 05/22/2020) (cit. on p. 9).

[13] Ministry of Environment and Food. *Bekendtgørelse om vandkvalitet og tilsyn med vandforsyningsanlæg*. URL: https://www.retsinformation.dk/eli/lta/2019/1070 (visited on 05/26/2020) (cit. on p. 21).

[14] V. Geissen et al. *Emerging pollutants in the environment: A challenge for water resource management*. 2015. URL: https://doi.org/10.1016/j.iswcr.2015.03.002 (cit. on p. 1).

[15] Jean-Claude Grivel. *Photocatalytic decomposition of industrial dyes using doped ZnO thin films - fall 2019* (cit. on pp. 7, 29, 42).

[16] P. Held. "Using the Cytation 5 Cell Imaging Microplate Reader to Monitor Cell Culture Status". In: *BioTek Instruments, Inc., Winooski, VT USA* (Mar. 22, 2018) (cit. on p. 21).

[17] *How do you calculate the appropriate flowrate?* URL: https://www.biosandfilters.info/faq/6b58ad89/how-do-you-calculate-the-appropriate-flow-rate-particularly-when-designing-a-non-standard-biosand-fi (visited on 05/27/2020) (cit. on p. 32).

[18] L. Huisman and W.E.Wood. "Slow Sand Filtration". In: (1974). URL: https://apps.who.int/iris/bitstream/handle/10665/38974/9241540370.pdf;jsessionid=42F6625A387E32B00938D%20588909386D9?sequence=1 (cit. on p. 4).

[19] Y. Kholin and N.M. Petrossyan. "Aggregation of Rhodamine B in Water". In: *Russian Journal of Applied Chemistry* 77 (Mar. 2004), pp. 414–422. DOI: 10.1023/B:RJAC.0000031281.69081.d0 (cit. on p. 10).

[20] *Kommunalt avløp, hydraulisk kapasitet*. URL: https://www.ssb.no/avlhyd/ (cit. on p. 30).

[21] K.R. Kunduru et al. *Nanotechnology for Water Purification: Applications of Nanotechnology Methods in Wastewater Treatment*. 2017. ISBN: 9780128043004; 9780128043714. DOI: 10.1016/B978-0-12-804300-4.00002-2 (cit. on p. 3).

[22] J. Laane et al. "Orientation and Optical Polarized Spectra (380–900nm) of Methylene Blue Crystals on a Glass Surface". In: *International Journal of Spectroscopy* (2013). ISSN: 1687-9449. DOI: 10.1155/2013/923739. URL: https://doi.org/10.1155/2013/923739 (cit. on pp. 5, 10).

[23] Yue-Sheng Li et al. "Interaction of coomassie brilliant blue G250 with human serum albumin: Probing of the binding mechanism and binding site by spectroscopic and molecular modeling methods". In: *Journal of Molecular Structure* 968.1 (2010), pp. 24–31. ISSN: 0022-2860. DOI: https://doi.org/10.1016/j.molstruc.2010.01.015. URL: http://www.sciencedirect.com/science/article/pii/S0022286010000396 (cit. on p. 5).

[24] S. Merouani et al. "Influence of Bicarbonate and Carbonate Ions on Sonochemical Degradation of Rhodamine B in Aqueous Phase". In: *Journal of hazardous materials* 175 (Oct. 2009), pp. 593–9. DOI: 10.1016/j.jhazmat.2009.10.046 (cit. on p. 5).

[25] Miljø-direktoratet. *Avløpsanlegg*. URL: https://www.norskeutslipp.no/no/Avlopsannlegg/?SectorID=100 (visited on 06/01/2020) (cit. on p. 30).

[26] Open.Food.Facts. URL: https://dk.openfoodfacts.org/additive/e133-brilliant-blue-fcf (visited on 05/22/2020) (cit. on p. 27).

[27] A. Ragab, I. Ahmed, and D. Bader. "Aggregation of Rhodamine B in Water". In: *Molecules* (Feb. 2019) (cit. on p. 5).

[28] A. Ragab, I.Ahmed, and D.Bader. "The Removal of Brilliant Green Dye from Aqueous Solution Using Nano Hydroxyapatite/Chitosan Composite as a Sorbent". In: *Molecules (Basel, Switzerland)* 24.5 (Feb. 2019). ISSN: 1420-3049. DOI: 10.3390/molecules24050847. URL: https://europepmc.org/articles/PMC6429269 (cit. on p. 10).

[29] D.D. Ratnayaka, M.J. Brandt, and K.M. Johnson. "Water Supply, Chapter 8, Filtration Granular Media Filtration". In: (2009). URL: https://doi.org/10.1016/B978-0-7506-6843-9.00016-0 (cit. on p. 4).

[30] A.T. Rebollo. *Role of Brilliant Green on the Detection and Seperation of Non-Chomoric Analytes by Reversed-Phase Liquid Chromatography (Dimerization)*. 1985. URL: http://hdl.handle.net/10150/275434 (cit. on p. 10).

[31] *Renseanlæg i Danmark*. URL: https://www.dingeo.dk/renseanlaeg/#?kommune=K%C3%B8benhavn%20kommune (visited on 05/29/2020) (cit. on pp. 30–32).

[32] S.Lo, H.Jeng, and C.Lai. "Characteristics and adsorption properties of iron-coated sand". In: *Water Science and Technology* 35.7 (1997). Adsorption in the Water Environment and Treatment Processes, pp. 63–70. ISSN: 0273-1223. DOI: https://doi.org/10.1016/S0273-1223(97)00115-7. URL: http://www.sciencedirect.com/science/article/pii/S0273122397001157 (cit. on p. 14).

[33] Shimadzu. *How does a spectrophotometer function?* URL: https://www.ssi.shimadzu.com/products/uv-vis-spectrophotometers/faqs/instrument-design.html (visited on 03/23/2020) (cit. on p. 8).

[34] Shimadzu. *The Relationship Between UV-Vis Absorption and Structure of Organic Compounds*. URL: https://www.shimadzu.com/an/uv/support/uv/ap/apl.html (visited on 03/28/2020) (cit. on p. 6).

[35] Sigma-Aldrich. URL: https://www.sigmaaldrich.com/catalog/product/sial/p3532?lang=en&region=DK (visited on 05/09/2020) (cit. on p. 5).

[36] Store.Danske.Leksikon. *Personækvivalent*. URL: https://denstoredanske.lex.dk/person%C3%A6kvivalent (visited on 05/29/2020) (cit. on p. 31).

[37] S. Swapp. *Scanning Electron Microscopy*. URL: https://serc.carleton.edu/research_education/geochemsheets/techniques/SEM.html (cit. on p. 9).

[38] Thermofisher. URL: https://assets.thermofisher.com/TFS-Assets/MSD/Scientific-Resources/FL53099-food-dyes-beers-law-qc-lesson-plan.pdf (visited on 03/20/2020) (cit. on p. 10).

[39] UN. *Envision2030 Goal 6: Clean Water and Sanitation*. URL: https://www.un.org/development/desa/disabilities/envision2030-goal6.html (visited on 06/06/2020) (cit. on p. 1).

[40] UNESCO. "Emerging Pollutants in Water Series". In: (2017). URL: https://www.helcom.fi/wp-content/uploads/2019/08/BSEP149.pdf (cit. on p. 3).

[41] UNESCO. "World Water Assessment Programme (WWAP)". In: (2019). URL: https://unesdoc.unesco.org/ark:/48223/pf0000367306 (cit. on p. 1).

[42] Vandetsvej. *Små og Store Vandværker*. URL: https://vandetsvej.dk/smaa-og-store-vandvaerker (visited on 05/05/2020) (cit. on p. 31).

[43] Visit.Denmark. *Avnsø Swimming Lake*. URL: https://www.visitdenmark.com/denmark/explore/avnso-swimming-lake-gdk917712 (visited on 05/24/2020) (cit. on pp. i, 3, 32).

[44] *Wastewater Treatment*. URL: https://stateofgreen.com/en/sectors/water/wastewater/wastewater-treatment/ (visited on 05/27/2020) (cit. on p. 30).

[45] M.J.M. Wells et al. "Emerging Pollutants". In: *Water Environment Research* 81.10 (2009), pp. 2211–2254. ISSN: 10614303, 15547531. URL: http://www.jstor.org/stable/29763384 (cit. on p. 3).

[46] WHO. *WHO Global Water, Sanitation and Hygiene, Annual Report 2018*. World Health Organization, 2018. URL: https://apps.who.int/iris/bitstream/handle/10665/327118/%20WHO-CED-PHE-WSH-19.147-eng.pdf (cit. on p. 1).

A Appendix

A.0.1 Chapter 4
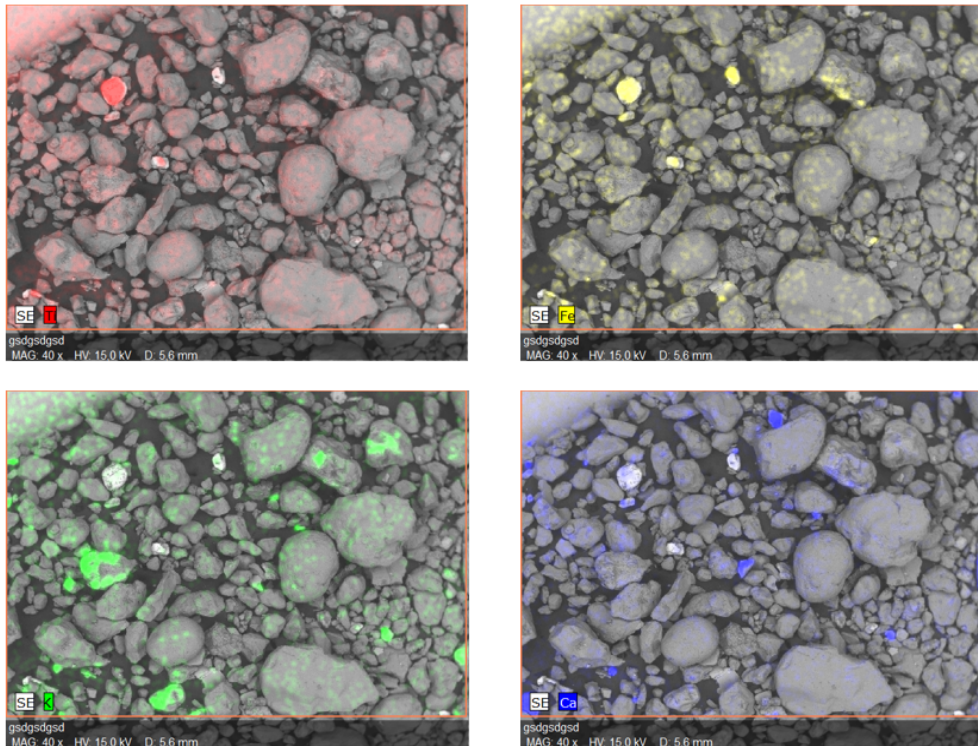**Investigating the Sand Samples**

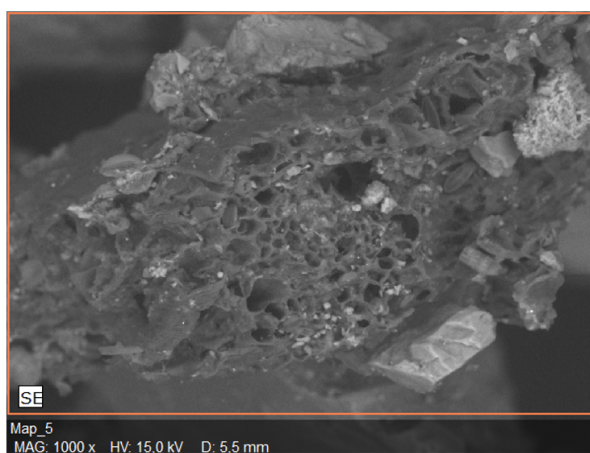Figure A.1: Elemental Map of Lake Sand from SEM

Figure A.2: SEM Picture of Porous Structure in Lake Sand. Mag 1000X.

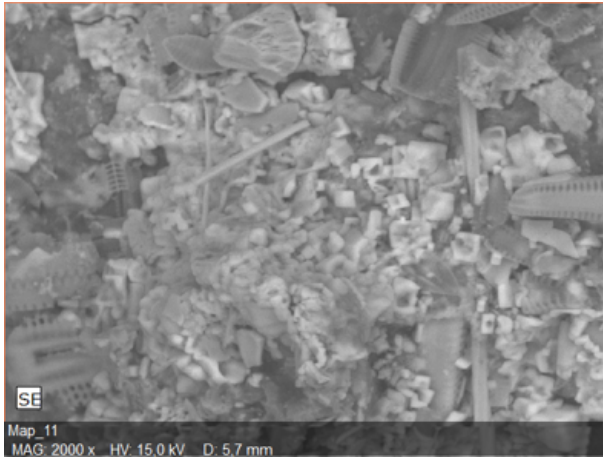Figure A.3: SEM Picture of Micro Organisms in Sea Sand. Mag 2000X.
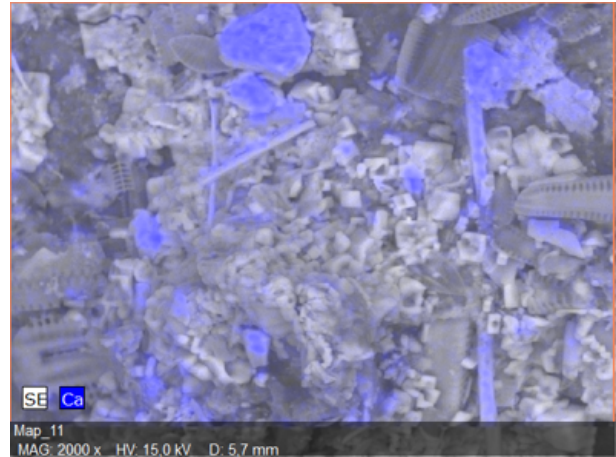
Figure A.4: SEM Picture of Sea Sand. Mag 2000X.

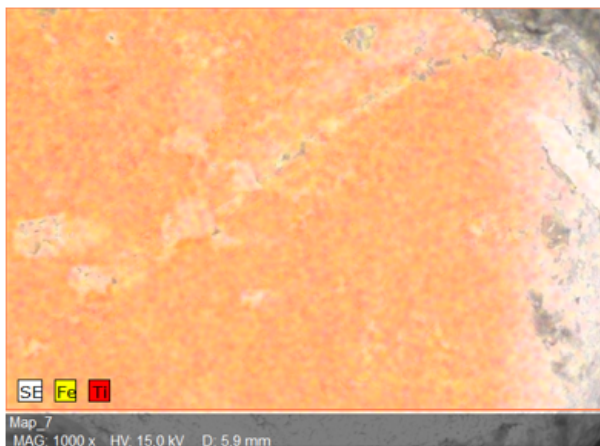Figure A.5: Elemental Map Of Calcium in Picture in Figure A.4

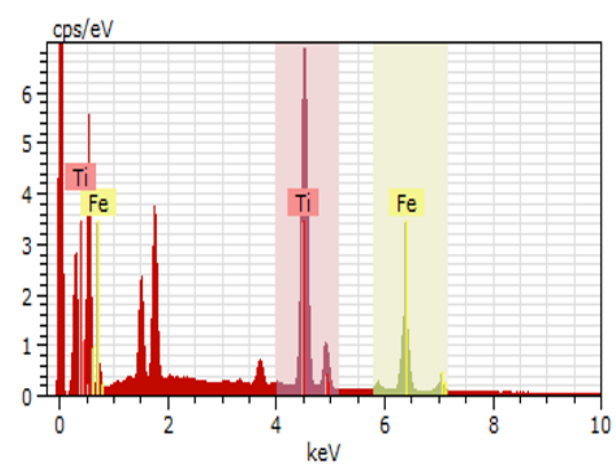Figure A.6: SEM Picture of Titanium and Iron Rich Grain in Lake Sand. Mag 1000X.

Figure A.7: Elemental Analysis of Iron and Titanium in Picture in Figure

A.6

First experiment: BB, BG, RB and PR in dried and 140◦Cheated lake sand with DI water
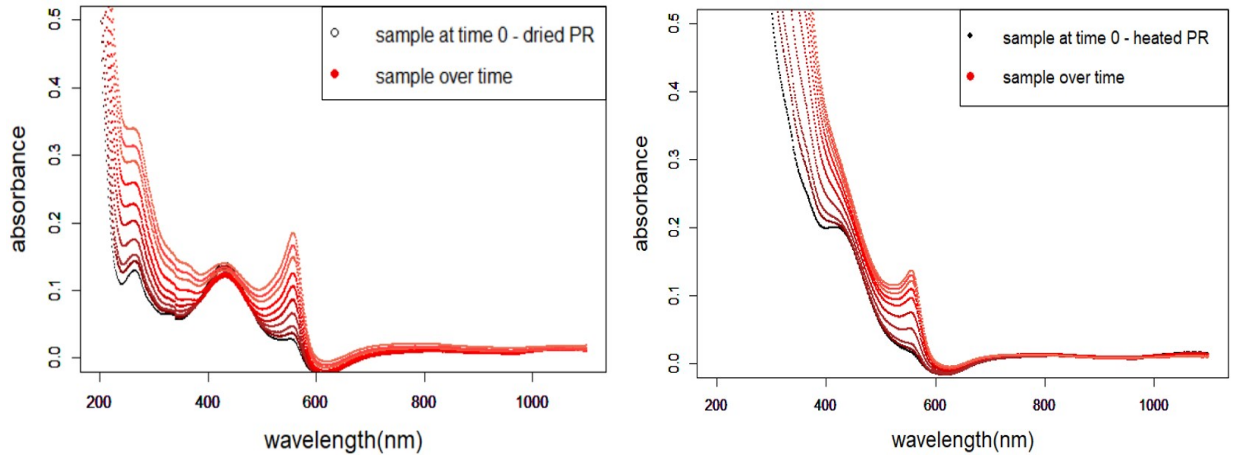
Figure A.8: Absorption Spectrum of Dried and Heated PR

Second experiment: MB in dried, 140°C and 500° lakes and with DI water
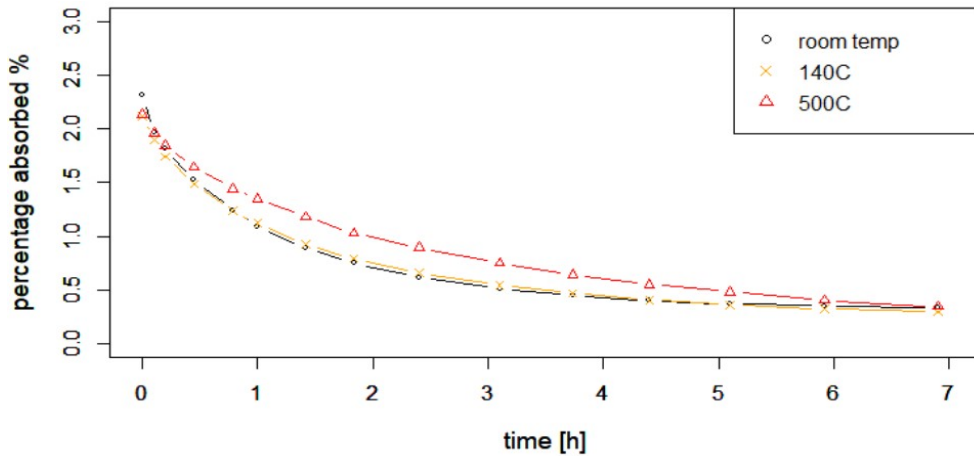
Figure A.9: Concentration of MB Over Time

Third experiment: BB and BG in Sea Water
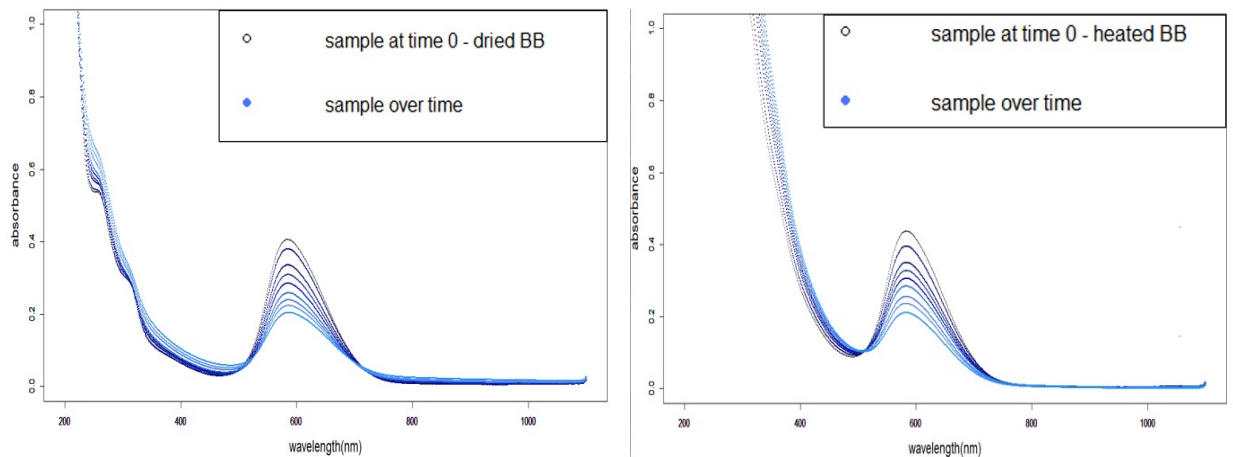
Figure A.10: Absorption Spectrum of Dried and Heated BB with Sea Water
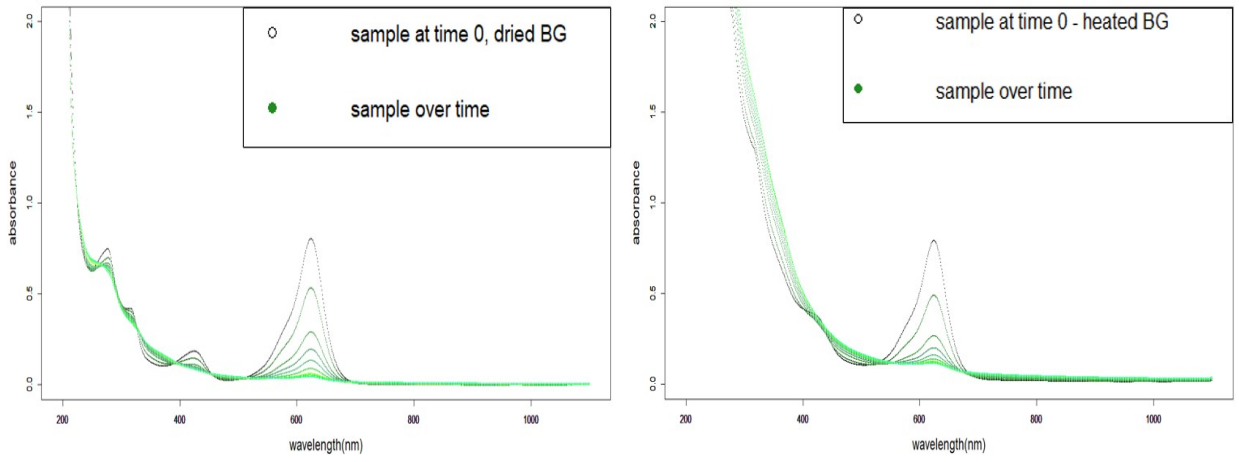
Figure A.11: Absorption Spectrum of Dried and Heated BG with Sea Water
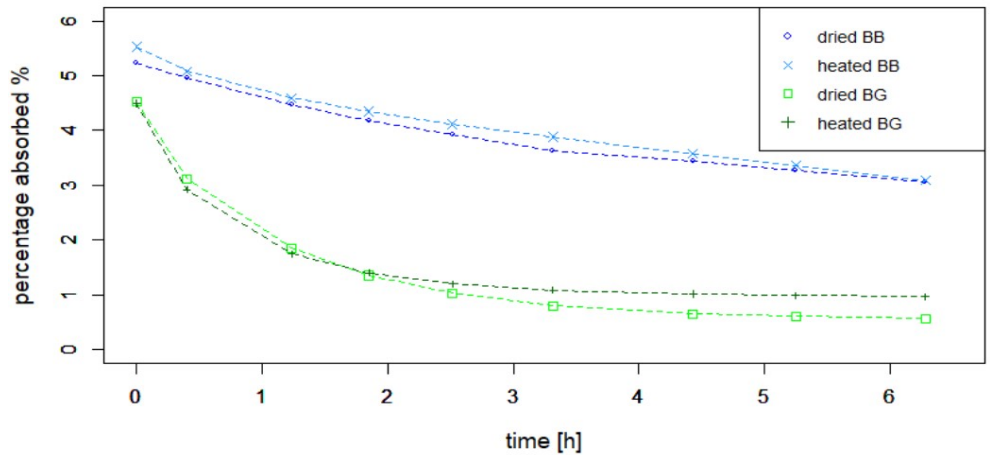
Figure A.12: Concentration of Dyes in Sea Water Over Time
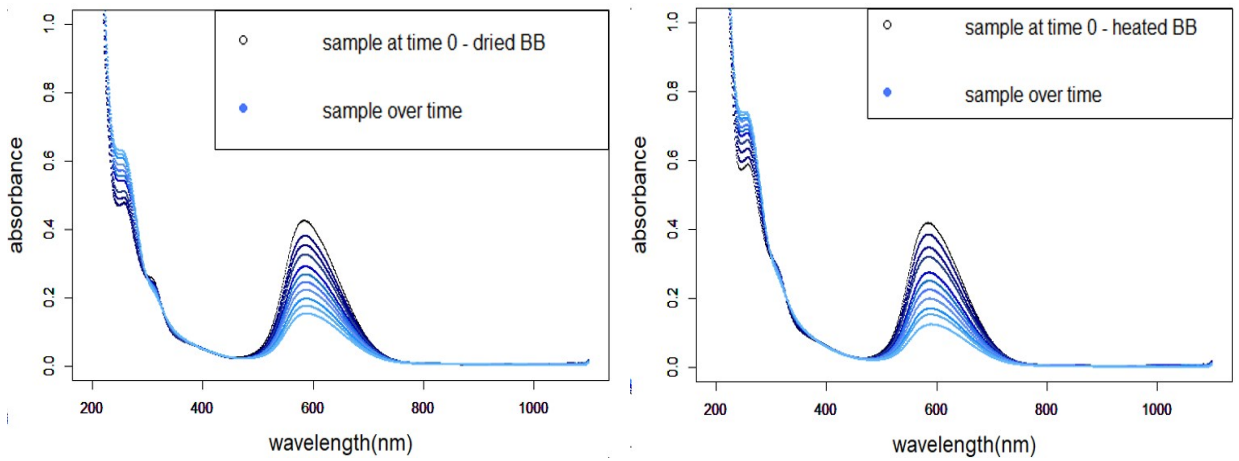
Fourth experiment: BB and BG in Sea Sand

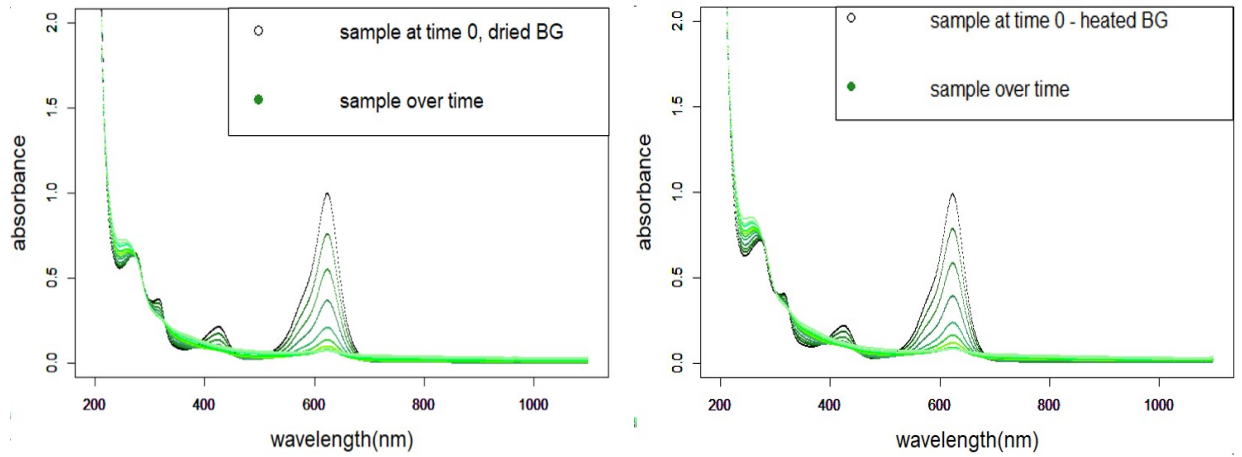Figure A.13: Absorption Spectrum of Dried and Heated BB with Sea Sand

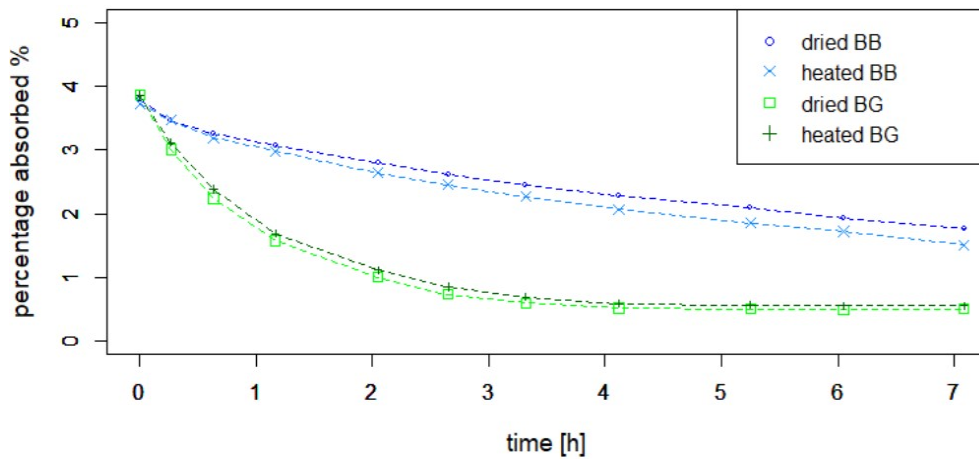Figure A.14: Absorption Spectrum of Dried and Heated BG with Sea Sand

Figure A.15: Concentration of Dyes in Sea Sand Over Time

A.0.2   Chapter 5 - Discussion
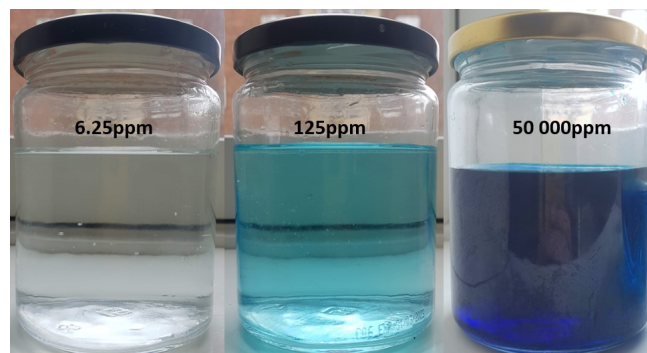**Investigating Uncertainties in Results**

Figure A.16: Jars of E133 of Different Concentrations at Start
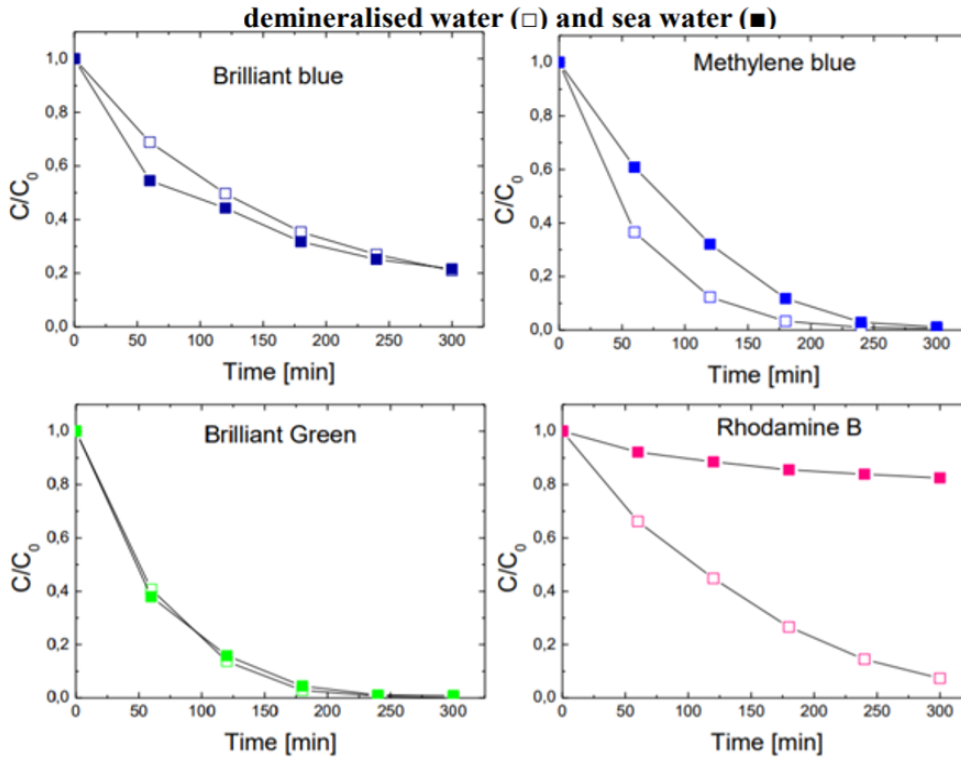
Photocatalysis Study Comparison

Figure A.17: Concentration Over Time for BB, MB, BG and RB in Photocatalysis [15]

A.0.3   Chapter 6 - Relevance for Commercial Water Purification in Scandinavia

Upscale Scenario

Area 44982 meters^2, 484185 feet^2 11.12 acres 0.017 miles^2 0.045 km^2
Perimeter 783 meters , 2567 feet 0.486 miles 0.783 km

Figure A.18: "Map Developer" Showing the Drawn Area and Belonging Data of Avnsø