CIE4040-09 Internship Report
Company and Personal Reflection

By

Carolina Nanni
5608945

April 2023

Master of Science Environmental Engineering
Faculty of Civil Engineering and Geosciences
Delft University of Technology

Internship
Conducted at DOPS Recycling Technologies bv

University Supervisor:	Prof. Merle de Kreuk
Company Supervisor:	Wiebe Pronker, DOPS Recycling Technologies bv

Table of Contents

1. Introduction

Between January 2023 and the beginning of March 2023, I conducted a full-time internship at DOPS Recycling Technologies bv. At the time of my internship, DOPS was a young start-up which had been founded two years prior (April 2021), and by the time I started my internship the four founders were in the process of constructing the laboratory scale test reactor, which eventually came into operation mid-way through March 2023 (hence after the end of my internship).

The present document includes the reflections concerning the employing company (Section 2) and personal learning goals (Section 3). A technical report including the results of my internship assignment is also included in this report.

Before starting the reflection, I would like to spend some words of thanks to my supervisors.

Firstly, I would like to thank the company team, Roeland Jan Dijkhuis, Harmen Oterdoom, Wiebe Pronker and Michiel Spits for welcoming me to join the project and offering me the opportunity to have this enriching internship experience. I would like to extend a special thanks to my day-to-day supervisor Wiebe Pronker, for his guidance and advice that helped me stay on the right working track and navigate the challenges of the internship, as well as the bright ideas and tips which were both informative and insightful to help me shape the internship.

Lastly, I would like to thank my university supervisor Merle de Kreuk for being interested in supervising this experience and providing essential advice and guidance for my laboratory work and in the internship agreement writing phase.

2. Company reflection

Company vision and work

DOPS Recycling Technologies bv is currently developing the Direct Carbon Immobilization (DCI™) thermochemical conversion technology for an innovative and sustainable approach to waste treatment and management. Their vision focuses on the recovery of energy, raw materials, and valuable resources from waste for meaningful reuse in industries, thus minimizing the environmental impact of waste while creating economic value.

Regarding the environmental impact, the DCI^{TM} technology which is being developed works by converting waste and biomass into syngas and sequestered carbon. The carbon material obtained is clean and safe to reuse in industries such as water treatment, whilst the syngas can be used to replace virgin fossil-based materials. Furthermore, the DCI^{TM} technology contributes to minimizing the impact of waste production and the issues connected to current waste management techniques, such as the carbon dioxide emissions from incineration and the methane emissions from landfilling.

From the economic point of view, when adopting the DCI^{TM} reactor companies can recover valuable material from the waste generated by their own process, thus effectively transforming their waste into value and creating a new source of revenue. Simultaneously, the technology allows companies to reduce their reliance on expensive waste disposal techniques. Furthermore, the DCI^{TM} technology can treat heterogeneous and polluted waste streams in the same reactor, making the technology easy to operate.

These are important aspects for the future development of waste treatment and management and as such DOPS is aiming at establishing itself in the waste management market by seeking partnership with companies and municipalities which are focused on reducing their carbon footprint and developing a circular economy through a more sustainable and cost-efficient management of waste. Waste-to-energy plants and industries focused on resource recovery are also potential stakeholders for the DCI^{TM} reactor.

DOPS' technology and vision are well-aligned with the current needs of the market, where the demand for innovative, sustainable, and cost-effective solutions for the waste issue are on the rise.

Company organization

By the time I started my internship, DOPS was a young start-up with its headquarters in the industrial centre of Velsen-Noord, in the province of North Holland, and an office in the technology incubator Yes!Delft located in Delft, South Holland. The office at Yes!Delft is however not regularly attended by the team, with the headquarters in Velsen-Noord being the main meeting location. At DOPS, the schedule for each team member is different every week, depending on the specific roles and projects. These would involve meetings with potential clients, partners, or stakeholders, which would take place either at DOPS' offices, at the partner's location, or online. I had the possibility to attend a few of these meetings throughout my internship, including the meeting with SNB (NV Slibwerking Noord-Brabant), a company which deals with the treatment of sewage sludge, and AVR, which deals with the treatment of different types of residual waste. Both are potential future clients for DOPS' technology, and attending these meetings provided me with an interesting insight on the company's business outlook and how DOPS' founders effectively communicate the benefits and advantages of their innovative technology to potential clients. Seeing the interaction between an engineering company and potential clients was an interesting experience for me as a first understanding of the business world and how it connects to engineering. Furthermore, attending these meetings allowed me to gain a better understanding of the current challenges and needs in the waste management industry, and how DOPS' technology aids in facing these.

The four founders of DOPS had extensive experience in different fields and at different types of companies before starting their work at DOPS. As a result, I had the feeling that albeit being a start-up, organizational-wise DOPS was quite structured considering its young age and compared to other startups which I have encountered. I found the technology itself also quite complex and detailed, which I also attributed to the experience of the founders. The four founders had divided the roles between them in the technical part and the business/economical part, and when they would attend meetings with other companies to present the DCI^{TM} technology, there would always be one representative of each role present. The different roles emerged during the weekly meetings in the decision-making process and would sometimes lead to challenges to reach a common viewpoint. At the same time, the diversity in the founder's backgrounds contributed to the different perspectives and approaches in problem-solving, ensuring well-informed decisions by the end.

Working environment

As mentioned, the schedule at DOPS was versatile, which kept every week exciting and dynamic. One constant in the team's weekly routine was the company meetings every Monday at the Velsen-Noord headquarters. Here, the plan for the week and the updates on ongoing projects were discussed. As an intern, I also participated in these meetings, and this helped me gain a better understanding of the company's operation, strategies, and struggles.

As a small start-up, the working environment at DOPS is very homogeneous, being the founders all Dutch men. As anticipated, I did not find this to be a limitation to the ideas and creativity of the team, owing to the different backgrounds of the founders. This was also my first internship experience; therefore, I do not have valuable comparisons measures with a more heterogenous team. As a non-Dutch intern, I did face some struggles with not knowing the native language, although I do not find that this hampered the outcome of my internship. I did struggle more with the fact that none of the founders were strictly operative in my sector, which sometimes made the reflection on results challenging. However, this was also overcome by the support of my university professors.

Throughout my internship, the only office I visited was the one in Velsen-Noord, and the rest of my internship was conducted in the Waterlab at TU Delft. The lab-scale reactor was not operational yet, so to produce more carbon material for my laboratory experiments, I had the opportunity to visit the laboratories at Gouda Refractories and make use of their furnaces. I was also fortunate enough to receive a tour of Gouda Refractories, which allowed me to visit a well-established company and see its full manufacturing process.

Towards the end of my internship, the lab-scale reactor came into operation at the InVesta Expertise Centrum in Alkmaar. I therefore had the opportunity to witness this important milestone for DOPS! I was able to see the first experiments conducted on the new technology and see the struggles, difficulties, and the excitement for the impact the DCI^{TM} technology will have in the future.

3. Personal Reflection

Personal learning objectives

Before starting my internship, I defined the personal learning objectives which I was hoping to acquire throughout the experience. Below is a summary of the learning goals I set before starting the internship, as stated in the internship learning agreement:

1) Gain knowledge in the waste management field.

2) Develop laboratory skills and use my university expertise to independently conduct experiments and analyze data.

3) Build capacities such as challenge facing and team-working.

4) Develop independent thinking and confidence in work.

For what concerns the first learning point, I feel like I have gained more knowledge than what I had before in the different methodologies used to treat waste, and the struggles involved in turning waste into value. Throughout the meetings I attended with DOPS at different waste-treatment companies, I had the possibility to understand the where the interests and challenges of the future waste management lies, and this also made clearer the importance of the development of the DCI^{TM} technology. On the other hand, I found it very complex to fully grasp the functioning of the DCI^{TM} reactor, and I attribute this to the chemical and thermodynamic concepts being quite far from what I've studied. However, the waste management field is a new sector for me and obtaining such a hands-on approach was a great opportunity to expand my knowledge in this area.

In regards instead to the development of my laboratory skills I definitely feel like the experience was successful and helped me gain a significant level of confidence in my laboratory knowledge. I feel much more capable of overcoming challenges that may arise during lab work and of identifying the correct resources to address issues that I may not know how to solve myself. By relying on my university knowledge to independently conduct my experiments I have developed confidence in myself as a student and as a researcher. In addition, delving deeper into the concepts I already knew in order to understand the outcome of my experiments also increased confidence in my research skills, critical thinking, and problem-solving abilities. Therefore, learning objective number four was also acquired. This was my first laboratory experience and as such I made a few mistakes in the initial execution and thought process while conducting experiments. I have learned from these and am confident in the approach and *status menti* I have developed for future experiences I will have in the lab.

Learning objective number three was correlated with undertaking an internship in a startup, where the environment is dynamic and vibrant and shaped by the everyday challenges associated with the development of a new technology. Despite being present at the headquarters of DOPS only once a week, I feel I have gotten an initial idea of the decision-making process and how priorities are established. I understood how tasks are divided amongst the team and how each team member has specific responsibilities based on their expertise, and I observed how the team works together to achieve the common goal of the company. This gave me valuable insight into how effective communication, collaboration and strong relationships between team members are essential for the successful outcome of a project. These considerations will be very valuable for my future career development.

Professional aspirations

In this section the professional aspirations, with regards to the company where the internship was completed at, are discussed.

I will start by saying that this was my first internship experience, and a very peculiar one as by the time I started, DOPS had been founded only two years prior. I was also the first intern working at DOPS. The experience I gained was probably very different to an internship conducted at a company which had been operative for a long-term. I got a lot of insight into the management and operation of a real-life project, including the development of the business plan and the organization of all aspects related to it. This was intriguing and an interesting addition to the smaller scale projects I have conducted at university.

With that being said, I believe I got less insight into the day-to-day life of a company, which I observed more during my visits to larger companies, especially at Gouda Refractories where I had the opportunity to return more than once and interact with different people across various departments.

I did not consider this a limitation however, and instead found it enriching to have such a diverse experience. After reflecting upon it, I believe I would actually find it quite exciting to have a similar role in my future career, upon gaining some experience in a large, established company. Working on a real-scale project such as the technology developed at DOPS is very stimulating, and the dynamic day-to-day schedule also keeps the work exciting. I realize that the struggles to set up a start-up are many, and I only experienced a few during my short time at DOPS. Therefore, I do believe that I would need to learn and gain more practical experience in the field, as well as a better understanding of finance and business.

Through my internship I have realized the importance of having a diverse set of skills, and that technical knowledge is not sufficient in order to succeed in the industry, especially one where interaction with co-workers and clients is essential. Observing the working of a startup has allowed me to witness firsthand the importance of having a basic understanding of financial knowledge, marketing, and strategic planning, as without these even the most innovative technology could struggle to progress.

This has motivated me to expand my skills in these sectors in order to become a well-rounded engineer and be able to constructively contribute to future projects.

Personal SWOT analysis

The final section of the personal reflection includes my individual assessment with my self SWOT (Strength, Weaknesses, Opportunities, Threats) analysis. The analysis is conducted according to the procedure described in the following link: https://ciccc.ca/blog/career-in-canada/swot-analysis-examples-students/#what-is-personal-swot-analysis

Strengths

- Interest for environmental sustainability challenges.
- Good communication skills and interaction with people, positive attitude and team energy.
- Rigorous and precise work.

Weaknesses

- Struggle with finishing work if I have no deadline.
- At times too detailed, which is very time-consuming.
- At times not confident enough to try completely new things.

Opportunities

- Good networking opportunities between my university and my internship.
- Relatively new and still growing master which will be needed to tackle issues in the future.
- Will take advantage of the growing global interest for sustainability-related problems.

Threats

- My time management skills have to improve overall.
- Am less confident about my abilities than my peers (but slowly improving!)
- Currently do not speak the local language (Dutch)

Impact of my role in the internship

As mentioned, the technology which is being developed by DOPS will be very significant for the future of the waste management sector by providing a sustainable and efficient method for treating waste.

Through my internship, I had the opportunity to work on an assignment that contributed to the further development of the technology. The results of my experiments provided valuable insight on the efficiency and effectiveness of the DCI reactor, and I believe this work will be useful in further optimizing the DCI^{TM} process.

I am pleased to have taken part in such an impactful project and look forward to seeing how the DCI^{TM} technology will continue to develop in the future.

Characterization and Performance Evaluation of Direct Carbon Immobilization (DCI^{TM})-Derived Carbon

CIE4040-09 Internship
Technical Report

By

Carolina Nanni
5608945

April 2023

Master of Science Environmental Engineering
Faculty of Civil Engineering and Geosciences
Delft University of Technology

Internship
Conducted at DOPS Recycling Technologies bv

University Supervisor:	Prof. Merle de Kreuk
Company Supervisor:	Wiebe Pronker, DOPS Recycling Technologies bv

Disclaimer: This report was prepared by students as part of the internship. While considerable effort has been put into the project, it is not the work of a licensed engineer and has not undergone verification that is common in the profession. The information, data, conclusions, and content of this report should not be relied on or utilized without thorough, independent testing and verification. University faculty members have been associated with this project as advisors, sponsors, or course instructors, but as such they are not responsible for the accuracy of results and conclusions.

Abstract

The present report aims at evaluating the results of carbon adsorption experiments conducted during my internship at DOPS Recycling Technologies bv. The internship started in January 2023 and lasted for a total of seven weeks, until March 2023.

The main task of the internship was evaluating the quality of the carbon produced by DOPS DCI^{TM} (Direct Carbon Immobilization) technology, and for this scope a series of laboratory experiments were conducted at the Waterlab of the Civil Engineering and Geosciences Faculty of TU Delft. Furthermore, Gouda Refractories allowed for the use of their SEM microscope to evaluate the surface of the carbon, due to difficulties with accessing the SEM-EDX microscope available at TU Delft.

This report includes a description of the specific carbon produced by the DCI^{TM} technology and used for the experiments. It includes the literature review utilised as background for my evaluations, the results, and discussions. Finally, recommendations are given for future studies that can be made as a continuation of the present research.

Highlights

- At low adsorbate concentrations, the carbon loading of the DOPS carbon is comparable to that of commercial Norit carbon.
- DOPS carbon exhibits faster kinetics than the Norit carbon.
- Throughout the batch adsorption experiments, the pH of the DOPS water decreases, whilst the Norit water increases.
- DOPS carbon has higher affinity than Norit for natural organic matter.

Abbreviations

DCI = Direct Carbon Immobilization (treatment and process)

GAC = granular activated carbon

MB = methylene blue

MW = molecular weight

NOM = natural organic matter

rpm = rate per minute

Table of Contents

1. Introduction

1.1. Background

DOPS Recycling Technologies bv, a start-up company founded in 2021, is currently developing the Direct Carbon Immobilization (DCI™) thermochemical conversion technology for the treatment of waste. The technology converts waste into a solid phase of carbon rich residue and small gaseous molecules for meaningful reuse in industries.

An important element in the development of the DOPS technology is the recovery and reuse of valuable raw materials. Therefore, it is important to evaluate the reusability of the building blocks which make up the waste treated by the DOPS DCI™ technology.

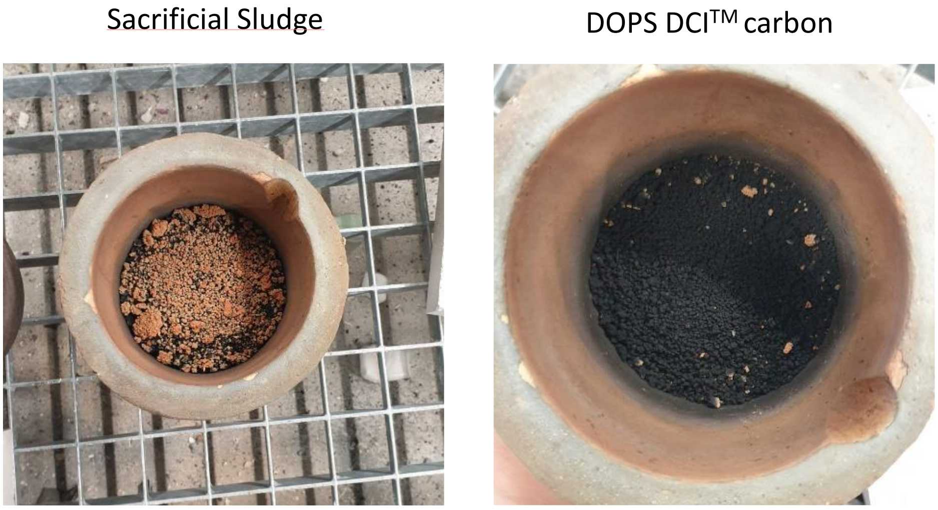
The aim of the internship, and the experiments conducted in the lab, is to *assess the quality and value of the solid residue recovered from the DOPS treatment of sewage sludge,* with specific regards to the characteristics of the carbon fraction recovered from the residue.

1.2. DOPS carbon

Traditionally, activated carbon is produced by subjecting carbon-rich material such as coal and wood to a double-step process to develop the physical and chemical properties required in the carbon structure to make the material adsorptive. The first step of the process is the carbonization of the material at 600-900°C in an inert atmosphere, usually nitrogen (Gupta & Afshari, 2009). The second step is the activation of the material, which can be physical (heating to 600-1200 °C with steam or oxygen) or chemical (heating to 450 – 900°C with addition of an acid). The activation process ensures the development of pores in the material surface (Thai et al., 2017), which leads to an increase of the specific surface area and the available adsorption sites, thus ensuring the material's adsorptive capacity.

The solid residue provided by DOPS for the experiment is derived from the DCI™ treatment of primary (aerobic) sewage sludge collected from the Limburg South Water Board. For the specific experiments of this research, DOPS did not yet have a laboratory reactor available, therefore a representative sample of solid residue was prepared using the sewage sludge provided by Limburg South Water Board and the furnaces available at Gouda Refractories. The conditions in the furnaces for the preparation of the solid residue mimicked the inside of the DOPS reactor, with the sludge being heated slowly to 1000°C followed by a slow cool down period. The material was held in containers made of refractory material with measures to avoid oxygen reaching the samples. The sewage sludge starting material was dried, but an oven test conducted at 120°C measured the moisture to still be 9% of the mass. After furnace treatment, the weight loss for the different containers ranged from 43% to 61% of the original mass.

Figure 1 (left) presents the solid residue remaining after the furnace treatment. The bright orange, superficial layer is referred to as the sacrificial sludge, and is the portion of material which was in contact with oxygen during the cooling of the furnace. As a result, the material is oxidized and red in color (due to the iron oxides). It is also more friable than the black solid residue. In Figure 1 (right) the sacrificial layer is removed and the material in the deeper layers is visible.



Sacrificial Sludge

DOPS DCI^{TM} carbon

Figure 1: Solid residue of WWTP sludge

This material, referred to as ‘DOPS carbon’ will be used for the experiments in this research.

Analysis done by DOPS prior to this research indicated that after furnace tests mimicking DOPS reactor, the recovered solid residue contained almost 10% in mass of carbon. Literature already indicates that sewage sludge can be reused as an adsorbent material after being subjected to different treatments (Otero et al., 2003). Therefore, assessing the quality and capacity of the carbon recovered by the new DCI^{TM} technology is an important step towards the advancement and further understanding of the technology.

1.3. *Research questions*

To understand the true value of the recovered components of DCI^{TM} treated sewage sludge, the internship will consist of laboratory experiments to determine the value of the solid residue. The research questions (in this report referred to as ‘RQ’) elaborated in this internship are the following:

RQ.1) Study the composition of the solid residue by evaluating the surface morphology (porosity, particle shape, size distribution) and the elemental composition of the carbon. Determine differences with commercial granular activated carbon.

RQ.2) Study the adsorption capacity of the DOPS carbon and evaluate the possibility of reuse in industrial processes. Compare the adsorption capacity between the carbon recovered with the DCI™ technology and standard commercial carbon.

RQ.3) Determine the extent of leaching of heavy metals from the DOPS carbon during adsorption.

2. Materials and Methods

2.1. Granular Activated Carbon (GAC)

Two different carbons are used for this research at the scope of comparing their adsorption capacities and morphological characteristics.

Norit GAC 830 P. (Cabot, ‘NORIT® GAC 830W’, February 2015) is used as commercial reference. As given in the Cabot datasheet, the particle size ranges between 2.36 mm and 0.6 mm. The Norit carbon is used as provided by the supplier.

The carbon recovered from the DOPS DCI^{TM} treatment (hereon referred to as ‘DOPS carbon’) was filtered through two sieves of 0.355 mm and 3.15 mm to obtain granules corresponding to the traditional particle size of granular activated carbon (GAC) of 0.3 – 3 mm. The choice of the sieves used for the filtering is based on the availability at the TU Delft Waterlab. On average, as seen in Figure 2, the Norit particles tend to be larger and more diversified in size than the DOPS carbon particles, which have a homogeneously distributed and overall smaller size.

Towards the end of the internship batch adsorption experiments were also conducted for the precursor DOPS material (hereon referred to as ‘Precursor DOPS’), so the primary sewage sludge prior to the DOPS DCI^{TM} treatment, dried to 91%. The grains of the precursor material are lighter in colour, more friable, and have a strong odour. The particles are on average larger than the material post-DCI^{TM} treatment.

Figure 2: Norit GAC 830 P. (left) and DOPS DCITM carbon (right)

2.2. RQ.1: Qualitative evaluation of the carbon porosity with SEM-EDX

2.2.1. Carbon porosity

Activated carbon is characterised by a highly porous surface surrounded by carbon atoms, which determine its adsorption capacities. The size and distribution of the pores is highly variable between different carbons, and together with the chemical composition on the surface of the carbon adsorbent, it determines how adsorption takes place inside the pores (Marsh & Rodríguez-Reinoso, 2006). Following the International Union of Pure and Applied Chemistry (IUPAC) nomenclature, carbon pore sizes are divided into (Pure Appl. Chem, pp 79):

- Macropores: pores size > 50 nm.
- Mesopore: pore size between 2 and 50 nm.
- Micropore: pore size smaller than 2 nm.

The distribution of the three types of pores on the surface and internal surface of the carbon determines the extent and types of pollutants that can be adsorbed, with larger, organic molecules that tend to be trapped on the carbon surface, where macropores are predominant, and smaller molecules that diffuse further into the carbon matrix occupying the micropores present in the internal carbon volume (Kemp, 2017). A combination of the three types of pore sizes and a high internal surface area ensures a carbon with high adsorption capacities and an affinity for a heterogeneous group of molecules.

2.2.2. Scanning electron microscope with energy dispersive X-ray spectroscopy (SEM-EDX)

A primary, qualitative evaluation of the adsorption capacity of a carbonaceous material is performed by evaluating the surface morphology of the carbon using electron microscopy.

Scanning electron microscopy (SEM) provides a direct method which is extensively used to study the microstructure of substances (Achaw, 2012b). Compared to indirect methods, SEM provides a direct view of the surface topography and as such a more accurate description of the pore shape and orientation. The drawback of this direct method, is that the evaluation of the surface porosity is only qualitative, compared to indirect methods such as mercury porosimetry which provide a quantitative value of the specific surface area of the activated carbon.

By observing both the external and internal surface of the DOPS carbon, it is possible to get an initial indication of the extent of the DCI^{TM} process in developing pores in the structure of the sewage sludge. This can facilitate in determining whether additional treatment, such as chemical activation, may be useful to attain a more developed pore structure of the DOPS carbon.

Pictures were taken and compared for DOPS material before and after treatment, Norit carbon and for the sacrificial sludge obtained by the Gouda experiments.

The SEM, as well as the EDX analysis, were conducted using the SEM JEOL JSM-6490LV available at Gouda Refractories. No additional pre-treatment of the carbon samples is required.

2.3. RQ.2: Evaluating the carbon adsorption capacity with batch adsorption experiments

2.3.1. Adsorbent: Methylene Blue

Methylene blue (CAS No: 61-73-4, MW = 319.85 gmol^{-1}) is a non- polar, synthetic, cationic, thiazine dye of molecular formula $C_{16}H_{18}ClN_3S$. It appears as a dark green powder when in solid phase and dark blue when in aqueous solution (Raposo et al., 2009). Upon dissolving in water, MB dissociates into a MB cation and a chloride anion. The molecular structure of MB is given in Figure 3 (source: Sigma Aldrich).

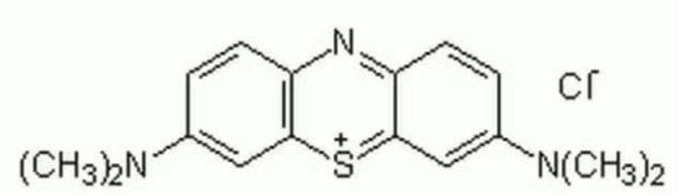


Figure 3: Methylene Blue molecular structure

MB is often used in adsorption experiments as its characteristic deep blue colour allows for a direct qualitative indication of the adsorption progression. Furthermore, its concentration in the water can be easily measured over time with the use of a spectrophotometer at wavelength 664 nm (Khudhair et al., 2020).

For the present research, two MB stock solutions are prepared (concentration stock solution (1) = 500 mg/L; concentration stock solution (2) = 2000 mg/L). The water matrix for both stock solutions is demi water.

Stock solution (1) is used to determine the MB calibration curve (Appendix A.2).

The two stock solutions are used for different adsorption experiments to obtain the desired mass ratios (initial MB mass/carbon mass) between the MB concentration and the carbon mass.

From stock solution (1), dilutions are performed to obtain solutions of starting MB concentration of 20 mg/L. From stock solution (2), dilutions are performed for an initial MB concentration of 200 mg/L.

An overview of the stock solutions and the correspondent dilutions is given in Appendix A.1.

2.3.2. Batch adsorption experiments: System set-up

Adsorption is a complex process resulting from the combination of several factors, including the properties of the adsorbent and adsorbate and composition of the water matrix. The surface area and pore system of the adsorbent, the molecular size and structure of the adsorbate, and the interaction between the adsorbate and the functional groups on the adsorbent surface all contribute to the adsorption. Determining the interaction between all these properties is complex, thus batch adsorption experiments are conducted to quantify adsorption performance.

The objective of the batch adsorption experiments in this research is to evaluate the performance of the DOPS carbon compared to commercial carbons in relation to methylene blue adsorption. Literature was referred to and adsorption experiments with commercial Norit ® GAC 830W were conducted to directly compare the adsorption capacity of the two carbons for identical experiments.

Batch adsorption tests are performed by adding a known amount of adsorbent in a volume of liquid with different doses of the adsorbate and keeping the solution in completely stirred conditions until the end of the experiment, which occurs when the adsorbent has reached adsorption saturation. The data collected is used to characterize the carbon by determining:

1) The adsorption isotherm curve which best represents the adsorption process and the values of the isotherm parameters.

   Adsorption isotherms represent the relationship between the portion of adsorbate in the water matrix and the portion adsorbed on the adsorbent surface at equilibrium and at constant temperature (Saleh, 2022). Adsorption isotherms provide details on the affinity between the specific absorbent and adsorbate, thus indirectly providing details on the interaction mechanisms and surface properties (Zhu & Chen, 2019). Once the isotherm curve is determined for the adsorption process, it is used in adsorption research and to optimize the use of adsorbents.

   Several isotherm models have been developed to understand the adsorption process; among these, the isotherm described by Freundlich (1906) and by Langmuir (1918) are the most commonly used for adsorption in liquid matrixes (Selmi et al., 2020b). The Freundlich isotherm is an empirical model, and the Langmuir is a mechanistic model based on the assumption that one molecule can adsorb per site (monolayer adsorption) and that neighbouring adsorption sites do not influence each other.

2) The kinetics of the carbon.

   The removal speed of contaminants from water is an important parameter when evaluating whether adsorption is feasible and whether the carbon can be used for industrial applications.

3) The carbon loading (q_e) for the specific adsorbate, to determine if the carbon adsorption capacity for methylene blue is competitive when compared to other commercially available carbons.

   Carbon adsorption capacity q_e, measured as (mg adsorbate/g adsorbent), measures the amount of adsorbate taken up by the adsorbent per unit mass of the adsorbent in equilibrium state (Mokhatab et al., 2019). It is specific for each adsorbent-adsorbate couple and provides the performance of different adsorbents for a specific contaminant.

   Rafatullah et al., 2010 provides an overview of the typical adsorption capacities of common activated carbons and coals for methylene blue adsorption. Values range from 10 to 900 mgMB/g, depending on the affinity of the specific carbon for the adsorbent and the physical-chemical changes of the material after activation.

The main experimental variables that influence the adsorption process are the temperature and the pH, with adsorption favoured at higher temperatures. The influence of the solution pH is dependent on the type of adsorbent. Being methylene blue a cationic dye, its adsorption is favoured at basic pH (Selmi et al., 2020c).

The system is composed of a digital orbital shaker where up to three laboratory bottles of 500 mL can be placed at the same time. The shaker is connected to a power supply and kept in constant shaking for the whole duration of the experiment, which can range from six hours to two days depending on the mass ratio between pollutant and carbon. The solution bottles are closed with a lid to prevent spills when shaking.

An overview of the system set-up is given in Figure 4.

Figure 4: Batch adsorption system set-up

2.3.3. Water Matrix

Both demi water and canal water are used in the adsorption experiments. Most experiments in this research are conducted with the use of demi water, which provides carbon adsorption results in optimal conditions for the target pollutant, being this the only pollutant present in the water sample. However, DOPS aims at reusing their treated carbon for adsorption of contaminants present in wastewater, with particular regard to adsorption of pharmaceuticals. Demi water is not representative of the chemical composition of a wastewater sample, nor of the competition for adsorption sites which occurs when many pollutants are present in the water sample, such is the case of wastewater. The original intention was to evaluate the adsorption capacity that the DOPS carbon had with common over-the-counter pharmaceuticals and whether this was comparable to the adsorption capacity measured for MB. However, this would have required the use of an additional technology (LC-MS) for the measurement of pharmaceuticals, making the project too complex for a seven-week internship.

Therefore, it was decided instead to evaluate the competition for adsorption sites occurring between natural organic matter (NOM) present in the water sample and the target pollutant, methylene blue. NOM includes a complex range of diverse organic pollutants with diverse properties, and is a common contaminant present in wastewater (Tran et al., 2015). Due to its larger particle size and its concentration in water samples in the range of mg/L, NOM preloading and pore blocking of the carbon pores is a common phenomenon in adsorption processes and can negatively influence the adsorption of target pollutants, including pharmaceuticals (De Ridder et al., 2011). Evaluating the extent to which methylene blue adsorption decreases when natural organic matter is present in the water can give a preliminary indication of the affinity of DOPS carbon with NOM and whether this may be an issue when using DOPS carbon for adsorption in wastewater.

Raw canal water collected from the TU Delft Waterlab is used to evaluate adsorption competition between the natural organic matter contained in the canal water and the objective adsorbent (methylene blue).

Natural organic matter can be in suspended or dissolved form. Among other methods, the NOM concentration in water is measured using a spectrophotometer at wavelength 254 nm and quartz cuvettes. This measurement method is used for the current research. As the collected sample for analysis is filtered before measurement, the spectrophotometer reading will provide values referring only to the dissolved portion of the NOM present in the canal water sample.

2.3.4. Experimental Conditions

The batch adsorption experiments in this research are carried out using 500 mL solution bottles and a digital orbital shaker running at 160 rpm. Every experiment is run until adsorption equilibrium is measured, identified by the MB concentration remaining constant over time.

The experiments are conducted using three different of carbon: the commercial Norit, the DOPS carbon after DCI^{TM} treatment (referred to as ‘DOPS carbon’) and the DOPS carbon prior to DCI^{TM} treatment (referred to as ‘Precursor DOPS’).

The solution bottles are prepared by diluting the appropriate stock solution to the desired initial MB concentration (Appendix A1). Dilutions are performed with demi water, and for experiment 4 (Table 1), they are also performed using canal water as the water matrix.

An overview of the experimental conditions is given in Table 1:

Table 1: Batch adsorption tests experimental conditions overview

Experiment	Mass ratio (g MB/g GAC)	Carbon Dose (g)	Initial MB concentration (mg/L)	Carbon type used	Expected time to reach equilibrium (hr)
1	0.4	0.025	20	- DOPS carbon - Precursor DOPS	24
2	0.04	0.25	20	- DOPS carbon - Norit - Precursor DOPS	24
3	0.01	1	20	- DOPS carbon - Norit - Precursor DOPS	20
4	0.004	2.5	20	- DOPS carbon - Norit	6
5	0.1	1	200	- DOPS carbon - Norit	48

Due to time availability, except for experiments 2 and 3 using DOPS carbon, the experiments were run only once.

The expected time to reach equilibrium was obtained from trial adsorption experiments conducted on DOPS carbon for experiments 1, 2 and 4.

2.3.5. Sampling and Measuring

The solution bottles are prepared by first diluting the MB to the desired initial concentration. The bottles are shaken on the orbital shaker for one minute at rpm 160 to evenly distribute the MB in the bottle, and a first sample (t_0) is collected to determine the exact initial concentration of the dye. The carbon is then added, and the experiment starts. Samples are collected with a 5 mL syringe and filtered with 0.2-micron filter to eliminate any carbon particles which may interfere with the spectrophotometer reading. The MB and NOM concentrations are measured using a UV-Vis Spectrophotometer at the desired wavelength (664 nm for MB absorption, 254 nm for NOM absorption). To not determine variations in the experimental conditions throughout the experiment, the volume of the collected samples must not exceed 10% of the initial solution volume. Considering the initial volume to be 500mL, and that the samples collected have a volume of 5mL, a maximum of ten samples can be collected for each individual experiment. Depending on the experiment and the expected time required to reach adsorption equilibrium (as given in Table 1), the collection of the ten samples is distributed throughout time for each experiment.

Throughout the adsorption experiment, the temperature is kept at room temperature (around 20°C) and the pH is monitored throughout time for specific experiments using a pH-meter.

The kinetic curve of the adsorption experiment is obtained plotting the pollutant concentration over time.

The isotherm equations for Freundlich and Langmuir are given in Table 2, along with the linearised equations used to calculate the parameters of the respective isotherm.

Table 2: Freundlich and Langmuir Isotherm equations

	Isotherm equation	*Linearised equation*
Freundlich	$q_e = K * \boldsymbol{C_e}^n$	$logq_e = logK + n * logC_e$
Langmuir	$q_e = \frac{(\boldsymbol{q_{max}} * \boldsymbol{b} * \boldsymbol{C_e})}{1 + b * C_e}$	$\frac{\boldsymbol{C_e}}{\boldsymbol{q_e}} = \frac{\mathbf{1}}{\boldsymbol{q_{max}} * \boldsymbol{b}} + \frac{\boldsymbol{C_e}}{\boldsymbol{q_{max}}}$

Where:

- q_e is the equilibrium loading capacity of the carbon (mg adsorbate/g adsorbent)
- Ce is the equilibrium concentration of the adsorbate in the aqueous phase (mg adsorbate/L)
- K is the Freundlich constant indicating the relative adsorption capacity of the adsorbent (mg adsorbate/g adsorbent) * (m^3/g adsorbate)^n
- n is the Freundlich constant indicating the intensity of adsorption. The higher the n, the more the adsorption is favourable for the adsorbate-adsorbent couple (g adsorbate/L)
- q_{max} is the monolayer adsorption capacity and gives information on the number of adsorption sites (mg adsorbate/g adsorbent).
- b is the Langmuir constant relating to the adsorption energy, and the reciprocal of the concentration at which the adsorbent reaches half of its saturation (L/mg adsorbate).

2.4. RQ.3: Carbon leaching using ICP-OES

2.4.1. Carbon Leaching

Sewage sludge absorbs heavy metals contained in wastewater due to biomass uptake. Heavy metals were measured in a smaller portion in DOPS carbon after DCI^{TM} treatment, The risk of heavy metal leaching from the carbon during adsorption processes in specific water conditions can cause issues in wastewater treatment plants. Assessing the heavy metal leaching from the DOPS carbon gives an important indication both for safety of use and to evaluate possibilities of recovery of the heavy metals contained in the carbon.

Traditional leaching tests would require for the carbon to be soaked for 24 hours in a solution of pH 4 of nitric acid (Townsend et al., 2003). The filtered solution is then measured for heavy metals using ICP-OES.

However, due to difficulties in accessing the nitric acid in the TU Delft Waterlab, the ICP-OES tests were conducted on the filtered water sample at the end of batch experiments on DOPS carbon. This was considered a reasonable approximation as it was observed that throughout the adsorption experiment using DOPS carbon, the pH in the solution dropped immediately from 5.5 (pH of methylene blue solution) to 4.5. Furthermore, the pH of wastewater, for which DOPS plans to use their carbon, ranges from 6 to 8. Water samples from batch experiments on DOPS carbon which had been soaked for at least 20 hours were considered an acceptable alternative for an initial indication on the extent of carbon leaching from the DOPS carbon.

2.4.2. Inductively coupled plasma – optical emission spectrometry (ICP-OES)

The presence of heavy metal in the water samples collected at the end of the adsorption experiments is determined with Inductively Couples Plasma – optical emission spectrometry (ICP-OES), which determines the presence and concentration of elements in water samples by creating a plasma and using a spectrometer. The principle on which the ICP-OES works is that heat from an argon plasma provides energy to the electrons. This induces the electrons to move from a neutral energy state to an excited state. When the electrons return to ground energy state, they release light at specific wavelengths. ICP-OES measures the amount of light emitted at each wavelength for the specific element, and correlates this to the concentration of element in the sample.

To conduct an ICP-OES analysis, it is necessary to provide values of expected initial concentrations for each of the elements. These were obtained from DOPS' analytical report and adapted for the ICP-OES measurement. Values can be found in the Appendix (A.9.1. for DOPS carbon and A.9.2. for the precursor material). The water samples were filtered with a 0.2-micron filter prior to ICP analysis.

An overview of the equipment and material used for the present research is given in Table 3.

Table 3: Overview of equipment and material used

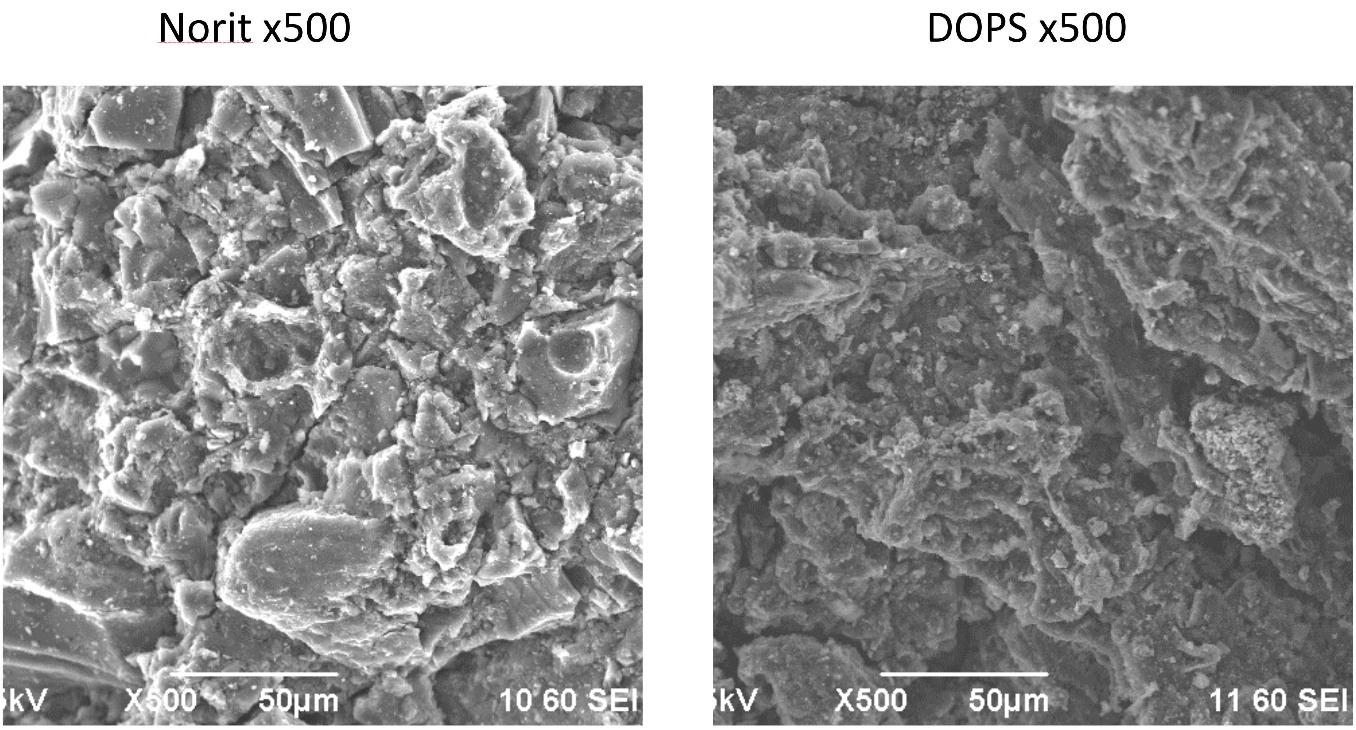
Equipment and Material	*Brand*
ICP -OES analyzer	Agilent 5800 ICP-OES with AVS valve and auto sampler
Digital Orbital Shaker	Heathrow Scientific
Magnetic stirrer	Labinco BV
Genesys UV- Vis Spectrophotometer	Thermo Scientific
Analytical scale AE 240	Mettler Toledo B.V.
500 mL laboratory bottles + cap	Thermo Scientific
WTW™ Multiparameter Benchtop Meter InoLab™ Multi 9630 IDS	Thermo Scientific
UV quartz cuvettes	Supelco

3. Results

3.1. SEM results

The SEM results are presented for the external and the cut-surface of the precursor material, the Norit and the DOPS carbon. The sacrificial sludge images are presented in Appendix A.7.5.

3.1.1. External Surface: Norit vs DOPS carbon



Norit x500

DOPS x500

Figure 5: Norit and DOPS carbon external surface

3.1.2. Cut surface: DOPS carbon

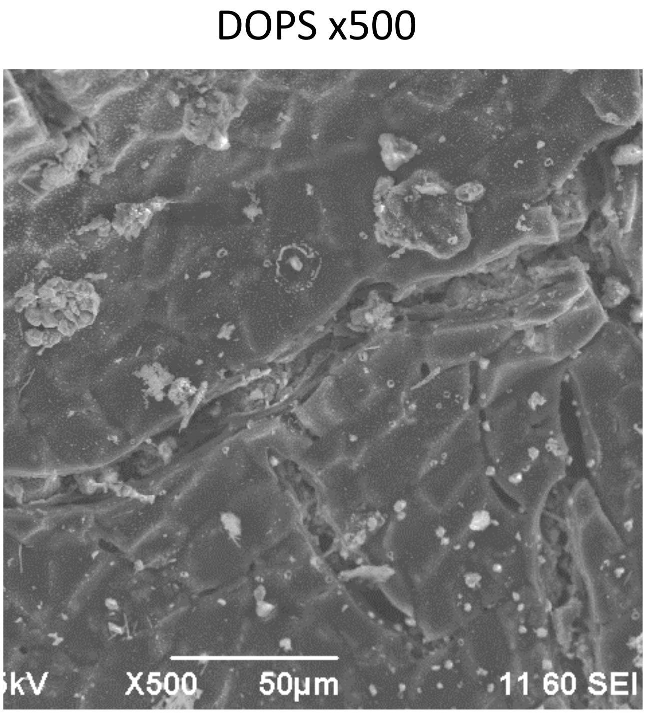
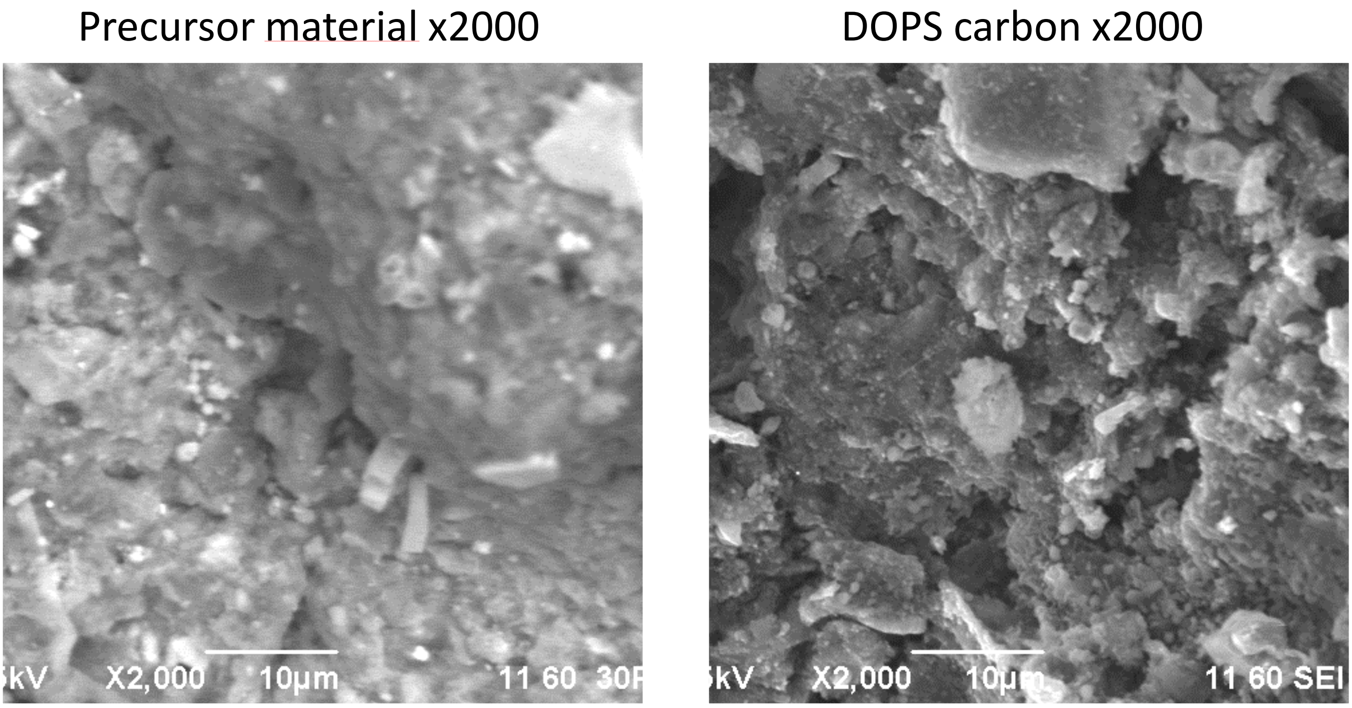

DOPS x500

Figure 6: DOPS carbon cut-surface

3.1.3. Cut surface: precursor material vs DOPS carbon


Precursor material x2000

DOPS carbon x2000

Figure 7: Precursor and DOPS carbon cut-surface

3.2. Batch adsorption experiments

3.2.1. Isotherm

A comparison of the performance of the three carbon types using demi water as water matrix is given in Table 4:

Table 4: Adsorption performance parameters overview (demi water as water matrix)

Experiment	*values*	*DOPS carbon*	*Norit*	*Precursor DOPS*
1	actual C_0	20	-	19.754
	C_e	16.475	-	15.474
	q_e	70.494	-	85.608
	$\eta_{removal}$	18%	-	23%
2	actual C_0	19.732	19.754	19.304
	C_e	4.37	3.230	3.581
	q_e	30.46	32.851	32.273
	$\eta_{removal}$	78%	84%	84%
3	actual C_0	19.033	19.271	19.574
	C_e	0.0	0.0	1.148
	q_e	9.517	9.636	9.310
	$\eta_{removal}$	100%	100%	95%
4	actual C_0	20	20.881	-
	C_e	0.0	0.72	-
	q_e	4	4.03	-
	$\eta_{removal}$	100%	97%	-
5	actual C_0	186.052	187.178	-
	C_e	108.329	35.788	-
	q_e	38.553	75.469	-
	$\eta_{removal}$	42%	81%	-

For DOPS carbon, replicates of experiment 2 and 3 were performed. Results are given in Appendix A.4.

The parameters obtained for Freundlich and Langmuir adsorption isotherm curves are given in Table 5 for the three carbons:

Table 5: Freundlich and Langmuir isotherm parameters

		DOPS	*Norit*	*precursor*
Freundlich parameters	$\mathbf{K_f}$	27.344	7.539	9.172
	n	0.073	0.712	0.844
Langmuir parameters	$\mathbf{q_{max}}$	38.988	102.495	217.345
	b	0.819	0.081	0.043

The isotherm representing methylene blue adsorption on DOPS carbon is given in Figure 8. The experimental data points (EDP) are numbered by experiment:

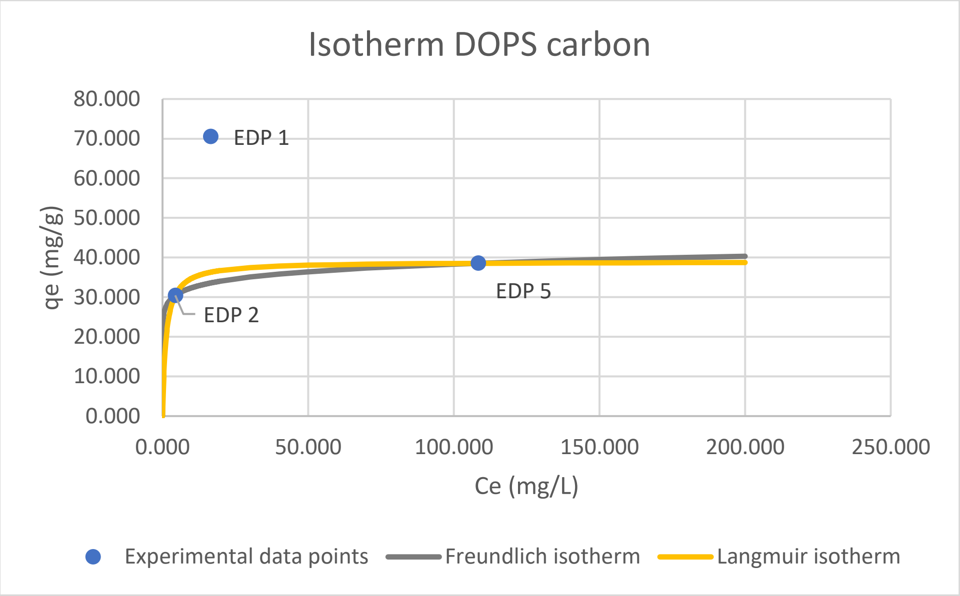


Figure 8: DOPS carbon methylene blue adsorption isotherm

3.2.2. Kinetics

A comparison of the adsorption kinetics for the three types of carbons is given in Figure 9. Methylene blue concentration over time was also evaluated to ensure that the MB did not decay; results are given in Appendix A.5.1.

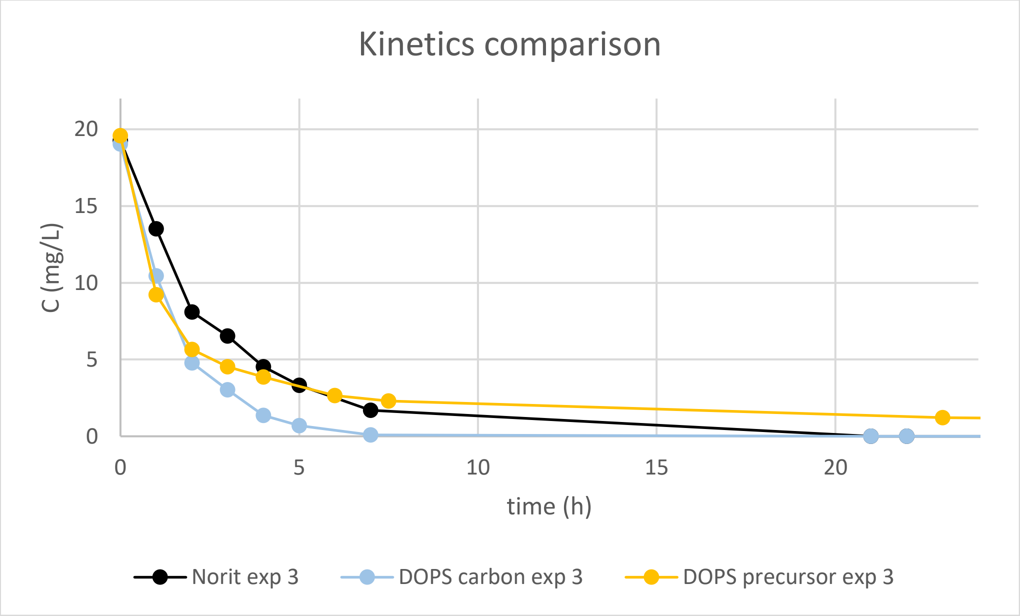


Figure 9: Carbon kinetics Comparison

3.2.3. pH trend

The comparison of the pH trend of the adsorption experiments for Norit and DOPS carbon, conducted both in canal and in demi water, is given in Figure 10.

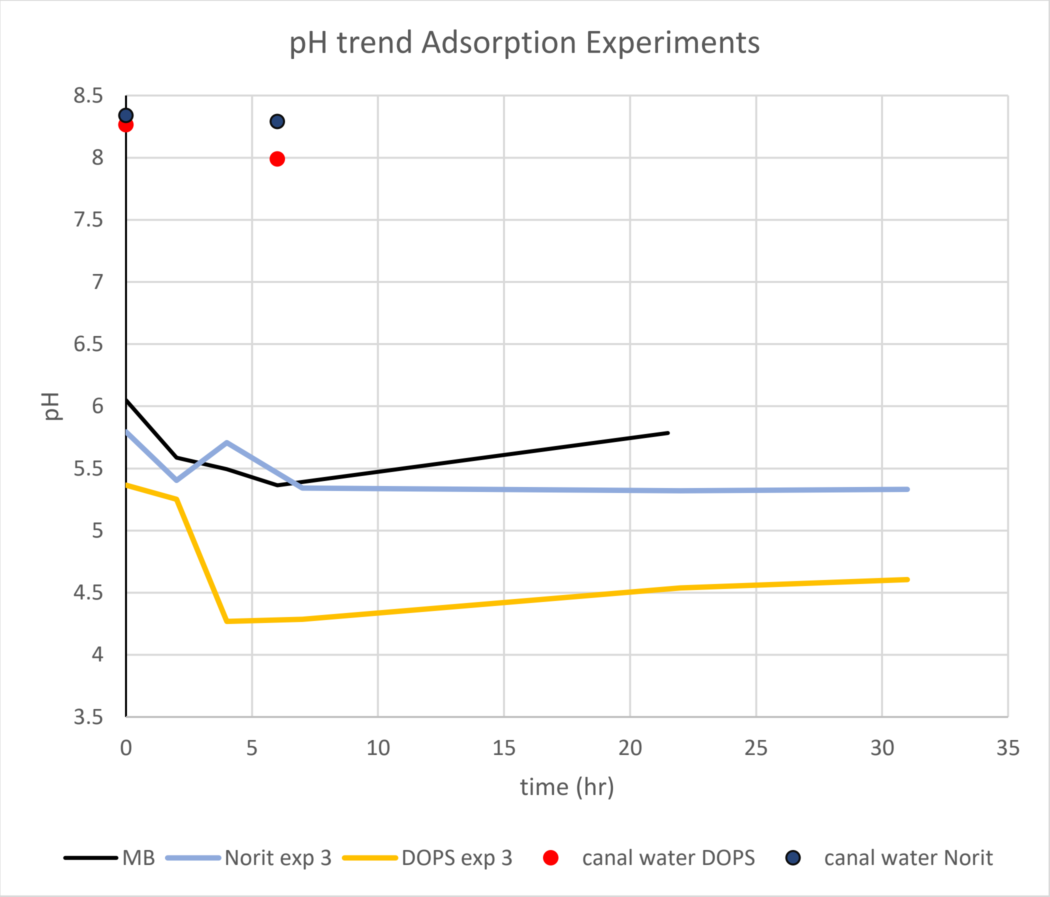


Figure 10: pH trend Adsorption Experiments

For DOPS carbon the pH was measured also for a second experiment 3 and for experiment 4 and confirmed the same trend as that given in Figure 4. An overview of all pH measurements is given in Appendix A.6.

3.2.4. Canal Water

The adsorption results for Norit and for DOPS carbon when using canal water are given in Table 6:

Table 6: Adsorption results for canal water

	EXPERIMENT	MB REMOVAL	NOM REMOVAL
NORIT	4	100%	18%
DOPS	4	100%	61%

The adsorption kinetics for both carbons when using canal water are given in Figure 11 and 12:

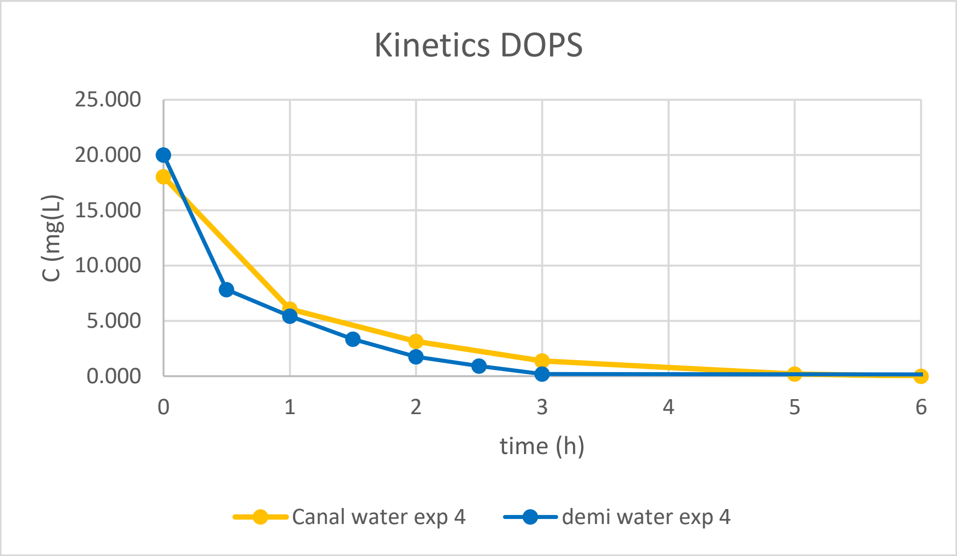


Figure 11: Kinetics DOPS carbon comparison with canal and demi water

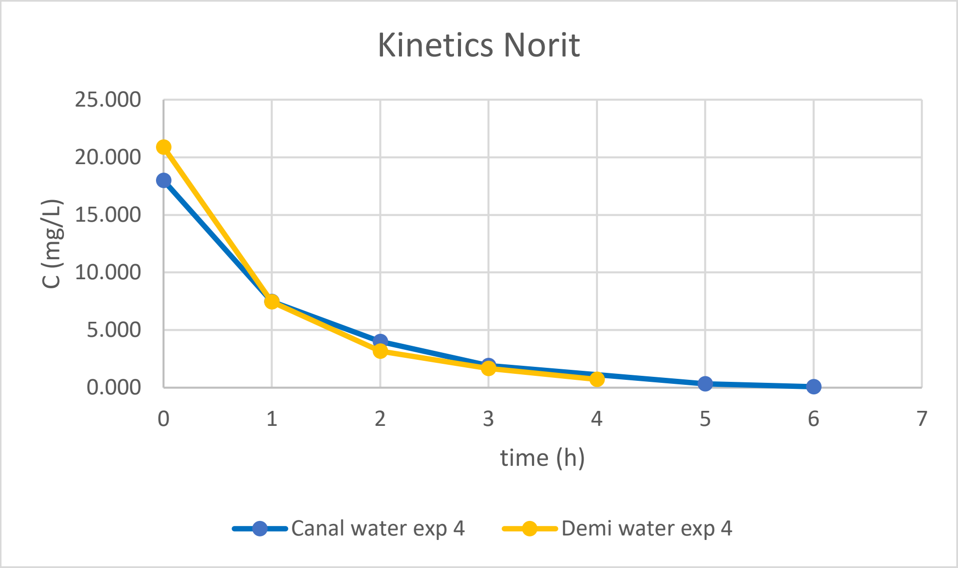


Figure 12: Kinetics Norit carbon comparison with canal and demi water

An overview of the performance of Norit and DOPS carbon when using canal water as the water matrix is given in Table 7:

Table 7: Adsorption performance parameters overview (canal water as water matrix)

Experiment	*values*	*DOPS carbon*	*Norit*
4	actual C0	18.042	17.997
	Ce	0.004	0.080
	qe	3.608	3.583
	$\eta_{removal}$	100%	100%

3.3 Leaching results

The leaching results for the DOPS carbon for the analyzed heavy metals (arsenic, chromium, copper, nickel, lead, and zinc) are given in Table 8.

Table 8: Leaching results DOPS carbon

Experiment	*soaking time (hr)*	*As average ppm*	*Cr Average ppm*	*Cu Average ppm*	*Ni Average ppm*	*Pb Average ppm*	*Zn Average ppm*
3	**31**	<0.025	<0.025	0.05	<0.025	<0.025	0.172
3	**54**	<0.025	<0.025	0.05	<0.025	<0.025	0.196
5	**51**	<0.025	<0.025	0.1	<0.025	<0.025	0.18

The leaching results for the precursor material for the analyzed heavy metals are given in Table 9:

Table 9: Leaching results precursor material

Experiment	*soaking time (hr)*	*As average ppm*	*Cr Average ppm*	*Cu Average ppm*	*Ni Average ppm*	*Pb Average ppm*	*Zn Average ppm*
1	**29**	0.002	0	0.01	0	0.003	0.01
2	**29**	0.001	0	0.04	0	0.003	0.01
3	**29**	0.004	0	0.05	0.01	0.002	0.02

4. Discussions

3.1. SEM – EDX results

The SEM images were captured at different magnifications to observe the pores on the surface and in the internal volume of the carbon. The magnification reached allowed for the measurement of the larger pores present on the surface of the two carbons. The analysis of the images revealed that the DOPS carbon has larger pores and in higher number when compared to the Norit. This differences can be attributed to the different manufacturing processes of the two carbons.

Furthermore, the observation of the cut-surface shows that the DOPS had a fragmented internal volume, with pores extending into the surface (Figure 6). Although they could not be measured directly, it is possible that the pores extend into micropores, which are the target pore dimensions for the adsorption of pharmaceuticals (Pavúková et al., 2022).

Clear pictures are obtained for DOPS solid residue and for the Norit, whilst the pictures from the sacrificial sludge and the precursor material are blurry and out of focus. This is due to the fact that the material in the sacrificial sludge and precursor is charging with electrons, deflecting the imaging electrons. Gouda Refractories limits the charging by coating the samples with carbon prior to observation with the SEM, thus making them conductive. The charging which characterizes the precursor material and the sacrificial sludge indicates a lower carbon portion on the surface of the carbon samples.

The EDX analysis are given in the attached document to this report.

3.2. Batch adsorption experiments

3.1.2. Isotherm and adsorption capacity

All three forms of carbon exhibit adsorption capacity to a higher or lower extent, which varies also depending on the mass ratios. The functional groups present on activated carbon usually determine a negatively charged surface (Van Oss, 1990), and the same has been found for sewage-sludge derived adsorbents (Graham et al., 2001), thus the cationic property of the MB adsorbent may have positively influenced the adsorption process.

The isotherm obtained for the DOPS carbon exhibited errors that would require further experimenting and evaluation. Specifically, there are discrepancies between the experimental data points and the fitted isotherm, therefore the isotherm parameters and values obtained for the DOPS carbon may not correspond to the precise values representing the carbon adsorption properties. The isotherm as presented in Figure 8 is fitted by excluding experimental data point 1 (EDP 1). The experimental data point was chosen as the most reasonable to exclude based on the fact that duplicates had been performed for EDP 2, and that by excluding EDP 5 and fitting the isotherm with the two remaining points, the adsorption capacity calculated for the carbon would be unrealistically high.

However, two data points are insufficient to plot an isotherm curve, therefore it is recommended to conduct further adsorption experiments in the range of high equilibrium concentrations (high mass ratios) to obtain a better fit of the isotherm.

The adsorption capacity q_e strongly depends on the carbonization and activation process of the carbon. Thai et al. (2017) calculated the methylene blue adsorption capacity of rice husk activated carbon to be 217.9 mg/g, whilst the adsorption capacity only reached 28.7 mg/g for the carbonized rice husk. Otero et al. (2003) also compared the results between pyrolyzed and chemically activated sewage sludges and only pyrolyzed sewage sludges and concluded that chemical activation aided in enhancing the creation and enlargement of pores. Further pretreatment of the DOPS material after the DCI^{TM} reactor could increase the internal surface and adsorption capacity of the DOPS carbon.

Chemical activation with the use of acid (i.e., phosphoric acid) (Johnson et al., 1999b), a base, a salt or and oxidant (i.e., bleach) can be considered.

From Table 4, it can be observed that for experiment 1, the adsorption capacity of the precursor material is higher than that of the treated carbon. This is also confirmed in the experiment conducted by Otero et al. (2003) on the adsorption capacity of MB of sewage sludge treated in three ways: only dried, dried and pyrolyzed, and dried and pyrolyzed and chemically enhanced. These experiments concluded that only dried sewage sludge demonstrated a higher adsorption capacity than both pyrolyzed and pyrolyzed and chemically enhanced carbons. For lower mass ratios in this research however, the adsorption capacity of the precursor material and of the treated carbon is almost equivalent. Therefore, the values obtained for experiment 1 may be outliers and are treated as such in the plotting of the isotherm.

With respect to the Langmuir isotherm parameters (Table 5), the q_{max} represents the maximum adsorption capacity of the adsorbent in relation to the adsorbate, whilst the b represents the strength of adsorption between the adsorbent and the adsorbate. The values obtained indicate that the precursor material exhibits a higher adsorption capacity than the DCI^{TM}-treated carbon, but the strength with which the MB is retained on the precursor material is lower. These results are in line with the results obtained by Otero et al (2003) for the methylene blue adsorption capacity of adsorbent material obtained by the sewage sludge in the three different forms (Table 10).

Table 10: Otero et al (2003) adsorption results obtained for sewage sludge adsorbent material in three different forms.

		only dried	*dried and pyrolyzed*	*dried, pyrolyzed and chemically enhanced*
Freundlich parameters	**K_f**	7.518	6.755	4.723
	n	2.096	4.766	4.155
Langmuir parameters	**q_{max}**	114.943	31.646	24.938
	b	0.03	0.0136	0.0198

3.1.3. Kinetics

It can be observed that the DOPS carbon has faster kinetics than that of the Norit. This can be explained by the smaller particle size of the DOPS carbon when compared to the particle size of the Norit. Therefore, the same sample mass for a DOPS carbon will contain more particles, and thus faster accessibility of the contaminants to more adsorption points. Additionally, the smaller the carbon particles, the easier mass transfer of the contaminants through the carbon occurs (Marsh & Rodríguez-Reinoso, 2006b).

Furthermore, observing the SEM pictures DOPS carbon appears to have a higher number of larger sized pores, indicating a better access of the contaminants to the adsorbent volume and a faster rate of adsorption (Kumar et al., 2019).

For the precursor material, it can be observed that initially the kinetics follows the one of the treated DOPS carbon, and then slows down. This may indicate an initial fast access of the contaminants to the adsorption points of the precursor material and would be explained by the very fractured structure which can be observed in the SEM images. Experiments conducted by Otero et al. (2003) indicate that only dried sewage sludge has faster kinetics than that of pyrolyzed sludge, but that is not observed in this case. What can be observed is that the kinetics of the precursor material slows down at around hour 4. This may indicate that all the available adsorption sites have been occupied by this time, and is confirmed by the precursor material reaching saturation capacity prior to the total removal of MB from the water in experiment 3.

Various kinetics models can be used to describe the kinetics of adsorption of the carbon. For methylene blue adsorption, second-order kinetic models are the most used, but the determination of the kinetic model was beyond the scope of this internship.

3.1.4. pH trend

Throughout the adsorption experiment, the pH in the Norit decreases slightly from 5.7 to 5.3, following the trend of the MB pH, and then remains stable at 5.3. The pH of the DOPS in methylene blue solution decreases from 5.3 to 4.6. This same trend was observed on repeated experiments for the DOPS carbon. Examples are given in Appendix A.6.

A possible explanation for the decrease of pH in the DOPS carbon may be the ferric oxide (Fe_2O_3) present in the ash of the carbon. If the iron occurs in the ash more as Fe(II) or as Fe(0), rather than as Fe(III), (which is to be expected because of the high temperature treatment in the presence of carbon, also the absence of the specific red color) then an oxidation process may take place during the experiment, inducing pH decrease (Equation 1):

Equation 1: Hypothesized iron oxidation process on DOPS carbon

$$3Fe(II) + O_2 + 10H_2O \rightarrow 4Fe(OH)_3 + 8H^+$$

3.1.5. Canal Water

Compared to commercial Norit carbon, DOPS carbon demonstrated a higher affinity for the natural organic matter contained in the canal water, removing up to 61% as opposed to Norit removal reaching 18%. This may be an indication that the functional groups on the surface of the DOPS carbon interact more with the natural organic matter, which is usually negatively charged (Sillanpää et al., 2015). However, as sewage sludge-derived adsorbents are usually negatively charged (Graham et al., 2001), the higher affinity is more probably correlated to the larger pores on the DOPS surface which better adapt to the size of NOM particles (Aschermann et al., 2018).

The DOPS kinetics of adsorption of methylene blue are slower when NOM is present in the water matrix, compared to the Norit kinetics which are stable for both water matrix. This further confirms the higher interaction of the DOPS carbon with the NOM.

3.2. Leaching tests

The ICP-OES measurements confirm that leaching occurs during the batch experiments. The extent of the leaching is more dependent on the soaking time of the carbon than on the higher methylene blue concentration (Experiment 5). Higher leaching values are observed for the treated material.

The maximum admissible values of heavy metal concentration in wastewater effluent are regulated by the World Health Organization and given in Table 11.

Table 11: Permissible limits (ppm) of heavy metals in wastewater (source: WHO)

Heavy Metal Ion	*Permissible Limit in WW effluent (ppm)*
arsenic	5
copper	2
lead	0.01
zinc	3
nickel	0.02
chromium	0.05

The operational time of a GAC in industrial processes can be years. Depending on the amount of carbon used and the volume of the GAC reactor, it is recommended that the leaching from the DOPS carbon is monitored, especially with regard to zinc and copper.

5. Recommendations for further testing

- Perform duplicate on DOPS carbon: as discussed, experiment 1 or experiment 5 (Table 4) for DOPS material may be an outlier. It is suggested to perform a duplicate to confirm the results and fit the isotherm with higher precision. Alternatively, performing additonal experiments with different mass ratios to further develop the isotherm of the DOPS carbon is recommmended. Mass ratios in the high range (higher than 0.1) should be analysed.

- Quantitative determination of the carbon specific surface area: the specific surface area (SSA) gives indication on the pore area available in the carbon, and is thus directly related to the adsorption capacity, with higher surface area indicating higher availability of adsorption sites (Iwuozor et al., 2021b). SSA also gives additional information on the kinetics of adsorption, with higher SSA indicating higher adsorption kinetics. Furthermore, SSA can also provide information on the pore sizes, as a higher SSA is correlated with the presence of micropores (Kumar et al., 2019). Calculating the SSA value with methods such as mercury porosimetry can provide useful information for further characterization of the DOPS carbon. The presence and extent of micropores and mesopores can also be measured with higher magnification electron microscopy and gas adsorption.

- Test the carbon performance for different types of contaminants: evaluate the adsorption capacity of the DOPS carbon for different types of contaminants and/or dyes of different characteristics with respect to molecular size and with respect to charge affinity; evaluate adsorption capacity of pharmaceuticals.

- Perform triplicates of experiments: to convalidate the results, especially in relation to the isotherms.

- Develop the Kinetics model of the carbon: Further evaluation of the carbon kinetics and adaptation to a kinetic model (i.e. Homogeneous Surface Diffusion Model or pore diffusion model). This can provide further detail on the mechanism of adsorption of the carbon (Krstić, 2021), and on other carbon parameters (Diffusion Coefficient) which can help predict how the carbon performs in different types of reactors.

- Column reactor tests. Batch adsorption experiments are an easily applicable experiment to obtain a preliminary idea of the characteristics of the carbon. However, they do not provide reliable results on how granular carbon will perform when used in industrial applications, where GAC is applied using column filters with continuous water flow. In this setting, the granular carbon is operated until complete exhaustion of its loading capacity, and the adsorbate diffusion through the carbon pores is favoured due to the lower water turbulence around the pores. Thus, better results both for kinetics and for carbon loading can be expected when conducting column tests, as opposed to shaken batch tests. Testing the DOPS carbon in column reactors can give a better indication on the effective carbon breakthrough, thus providing further information for characterizing the effective performance of the granular carbon.

6. Recommendations for DOPS Recycling Technologies

- Additional pre-treatment of the DOPS carbon before using it as an adsorbent can further increase the adsorption capacity. DOPS carbon underperforms compared to commercial carbons when the adsorbate concentration is much higher than the adsorbent mass. Thai et al., 2017 indicates that thermal (with oxygen at high temperatures) or chemical activation (with acid, salt or oxidant) further enhances the porous structure of activated carbon, thus increasing the number of adsorption pores in its surface and its overall adsorption capacity. Otero et al. (2003) confirms that the adsorption capacity of a chemically activated pyrolysed sludge is higher than that of the equivalent material which is only pyrolysed. Considering an activation step can make DOPS carbon more competitive with other carbons available on the market.

7. Conclusions

The research done throughout this internship aimed at evaluating the quality standards of the DCI^{TM}-recovered carbon from the thermochemical reactor under development at DOPS Recycling Technologies. Results are compared with the performance of commercially available carbon, and conclusions are drawn on the possibility of reuse of the DCI^{TM}-carbon in the wastewater industry and recommendations to improve the adsorption efficiency.

SEM-EDX analysis conducted to evaluate the surface morphology of the carbon highlights the presence of a porous structure both on the surface and in the internal volume of the carbon. Larger sized pores appear more common for the DCI^{TM}-carbon when compared to commercially available Norit carbon.

Batch adsorption experiments confirm the adsorption capacity of the DCI^{TM}-carbon. When comparing the performance with that of commercial Norit GAC 830 P, the DCI^{TM}-carbon exhibits comparable adsorption at lower mass ratios, whilst at higher mass ratios the DCI^{TM}-carbon underperforms, highlighting the need for further treatment to enhance the porous structure of the carbon and increase the available adsorption sites. Chemical activation is proposed as a possibility. The DCI^{TM}-carbon exhibits a faster adsorption kinetics than Norit; this is attributed to the smaller particle size which the DOPS carbon acquires during the thermochemical treatment. Lastly, the DOPS carbon displays a higher affinity for natural organic matter, which can be attributed to the chemical surface characteristics of the DOPS carbon or to the larger pores observed in the SEM analysis which are more compatible with NOM particle dimensions.

The precursor material demonstrates similar kinetics to the DCI^{TM}-treated material but reaches saturation faster, thus evidencing the lower number of available adsorption sites available in its structure. At lower mass ratios, the treated material performs better than the raw sewage sludge and accomplishes complete removal of the contaminant while the raw material does not. At higher mass ratios however, the precursor material performs better than the DCI^{TM}-treated carbon, confirming literature experiments which state that sewage sludge which is only dried performs better than thermally and chemically treated sewage sludge. More extensive analysis on the performance at higher mass ratios of the raw and treated material is needed to develop conclusions.

The leaching tests confirm zinc and copper leaching from the DOPS carbon at pH value of 4.5. The leaching of the other metals present in the carbon are negligible for the carbon mass and solution volume used. Higher leaching occurs for the DOPS carbon after treatment.

References

DOPS DCI Reconnaissance, Results of the research and work carried out in the context of the P>Act Plastic Challenge 2021, November 2022

Achaw, O. (2012b). A Study of the Porosity of Activated Carbons Using the Scanning Electron Microscope. *InTech EBooks*. https://doi.org/10.5772/36337

Aschermann, G., Zietzschmann, F., & Jekel, M. (2018). Influence of dissolved organic matter and activated carbon pore characteristics on organic micropollutant desorption. *Water Research*, *133*, 123–131. https://doi.org/10.1016/j.watres.2018.01.015

Cabot Corporation, NORIT® GAC 830W datasheet, February 2015

De Ridder, D., Verliefde, A., Heijman, S. G., Verberk, J., Rietveld, L. C., Van Der Aa, L. T. J., Amy, G. L., & Van Dijk, J. G. (2011). Influence of natural organic matter on equilibrium adsorption of neutral and charged pharmaceuticals onto activated carbon. *Water Science and Technology*, *63*(3), 416–423. https://doi.org/10.2166/wst.2011.237

Graham, N. M., Chen, X., & Jayaseelan, S. (2001). The potential application of activated carbon from sewage sludge to organic dyes removal. *Water Science and Technology*, *43*(2), 245–252. https://doi.org/10.2166/wst.2001.0096

Gupta, B. B., & Afshari, M. (2009). Tensile failure of polyacrylonitrile fibers. *Elsevier EBooks*, 486–528. https://doi.org/10.1533/9781845696801.2.486

Iwuozor, K. O., Ighalo, J. O., Emenike, E. C., Igwegbe, C. A., & Adeniyi, A. G. (2021b). Do Adsorbent Pore Size and Specific Surface Area Affect The Kinetics of Methyl Orange Aqueous Phase Adsorption? *Research Square (Research Square)*. https://doi.org/10.21203/rs.3.rs-777328/v1

Johnson, P. J., Joseph, S. D., & Williams, R. (1999b). Activated Carbon for Automotive Applications. *Elsevier EBooks*, 235–268. https://doi.org/10.1016/b978-008042683-9/50010-8

Kemp, Terence. (2017). A Brief 100 Year History of Carbon. Science Progress. 100. 293-298. https://doi.org/10.3184/003685017X14994318577435

Khudhair, A. K., Sherazi, S. T. H., & Al-Baiati, M. N. (2020). Adsorption of methylene blue from aqueous solutions by using a novel nano co-polymer. INTERNATIONAL CONFERENCE OF NUMERICAL ANALYSIS AND APPLIED MATHEMATICS ICNAAM 2019. https://doi.org/10.1063/5.0027741

Krstić, V. (2021). Role of zeolite adsorbent in water treatment. *Elsevier EBooks*, 417–481. https://doi.org/10.1016/b978-0-12-821496-1.00024-6

Kumar, P. A., Korving, L., Keesman, K. J., Van Loosdrecht, M. C., & Witkamp, G. (2019). Effect of pore size distribution and particle size of porous metal oxides on phosphate adsorption capacity and kinetics. *Chemical Engineering Journal*, *358*, 160–169. https://doi.org/10.1016/j.cej.2018.09.202

Liu, L., Luo, X., Ding, L., & Luo, S. (2019). Application of Nanotechnology in the Removal of Heavy Metal From Water. *Elsevier EBooks*, 83–147. https://doi.org/10.1016/b978-0-12-814837-2.00004-4

Marsh, H., & Rodríguez-Reinoso, F. (2006). Characterization of Activated Carbon. *Elsevier EBooks*, 143–242. https://doi.org/10.1016/b978-008044463-5/50018-2

Mokhatab, S., Poe, W. A., & Mak, J. Y. (2019). Natural Gas Dehydration and Mercaptans Removal. *Elsevier eBooks*, 307–348. https://doi.org/10.1016/b978-0-12-815817-3.00009-5

Otero, M., Rozada, F., Calvo, L., García, A. G., & Morán, A. (2003). Kinetic and equilibrium modelling of the methylene blue removal from solution by adsorbent materials produced from sewage sludges. *Biochemical Engineering Journal*, *15*(1), 59–68. https://doi.org/10.1016/s1369-703x(02)00177-8

Pavúková, D., Fašková, L., Melníková, E., Kubiňáková, E., Híveš, J., Štibrányi, L., Hudec, P., Naumowicz, M., & Gál, M. (2022). Removal of Environmentally Harmful and Hardly Degradable Pharmaceuticals Sulfamethoxazole, Diclofenac, and Cetirizine by Adsorption on Activated Charcoal. Water, 14(24), 3988. https://doi.org/10.3390/w14243988

Pure Appl. Chem., 1976, Vol. 46, No. 1, pp. 71-90. http://dx.doi.org/10.1351/pac197646010071

Rafatullah, M., Sulaiman, O., Hashim, R., & Ahmad, A. (2010). Adsorption of methylene blue on low-cost adsorbents: A review. *Journal of Hazardous Materials*, *177*(1–3), 70–80. https://doi.org/10.1016/j.jhazmat.2009.12.047

Raposo, F. S., De La Rubia, M., & Borja, R. (2009). Methylene blue number as useful indicator to evaluate the adsorptive capacity of granular activated carbon in batch mode: Influence of adsorbate/adsorbent mass ratio and particle size. Journal of Hazardous Materials, 165(1–3), 291–299. https://doi.org/10.1016/j.jhazmat.2008.09.106

Saleh, T. A. (2022). Isotherm models of adsorption processes on adsorbents and nanoadsorbents. *Elsevier EBooks*, 99–126. https://doi.org/10.1016/b978-0-12-849876-7.00009-9

Selmi, T., Seffen, M., & Celzard, A. (2020b). Effect of the adsorption pH and temperature on the parameters of the Brouers–Sotolongo models. *Environmental Science and Pollution Research*, *27*(19), 23437–23446. https://doi.org/10.1007/s11356-018-3835-8

Sillanpää, M., Matilainen, A., & Lahtinen, T. (2015). Characterization of NOM. *Elsevier EBooks*, 17–53. https://doi.org/10.1016/b978-0-12-801503-2.00002-1

Thai, H., MA, Ly, H. Q., Ho, V. A., Pham, N. C., Nguyen, D. Q., Vo, K. T. X., & Tuan, P. D. (2017). EFFECT OF THE CARBONIZATION AND ACTIVATION PROCESS ON THE ADSORPTION CAPACITY OF RICE HUSK ACTIVATED CARBON. *Vietnam Journal of Science and Technology*, *55*(4), 494. https://doi.org/10.15625/2525-2518/55/4/9124

Townsend, T., Jang, Y. C., Tolaymat, T., & Department of Environmental Engineering Sciences, University of Florida. (2003, March). *A Guide to the Use of Leaching Tests in Solid Waste Management Decision Making*. Retrieved April 19, 2023, from https://semspub.epa.gov/work/09/1112378.pdf

Tran, N. Q., Ngo, H. H., Urase, T., & Gin, K. Y. (2015). A critical review on characterization strategies of organic matter for wastewater and water treatment processes. *Bioresource Technology*, *193*, 523–533. https://doi.org/10.1016/j.biortech.2015.06.091

Van Oss, C. J. (1990). A review of: "Active Carbon." R.C. Bansal, J.B. Donnet and F. Stoeckli; Marcel Dekker, New York, 1988. pp. 482, $135.00. *Journal of Dispersion Science and Technology*, *11*(3), 323. https://doi.org/10.1080/01932699008943255

Zhu, K., & Chen, C. (2019). Application of nZVI and its composites into the treatment of toxic/radioactive metal ions. *Interface Science and Technology*, 281–330. https://doi.org/10.1016/b978-0-08-102727-1.00006-6

Appendix

A.1 Methylene Blue Stock solutions and Dilutions

A.1.1. Methylene Blue stock solution 1

Stock solution 1				
volume stock solution **1** (L)	Mass MB (g)	MB concentration stock solution 1 (g/L)	pH	Temperature (°C)
1	0.5	***0.5***	***5.062***	***15.7***

A.1.2. Methylene Blue stock solution 2

Stock solution 2		
volume stock solution 2 (L)	Mass MB (g)	MB concentration stock solution 2 (g/L)
0.5	1.0	***2***

A.1.3. MB dilutions: preparation of solution bottles

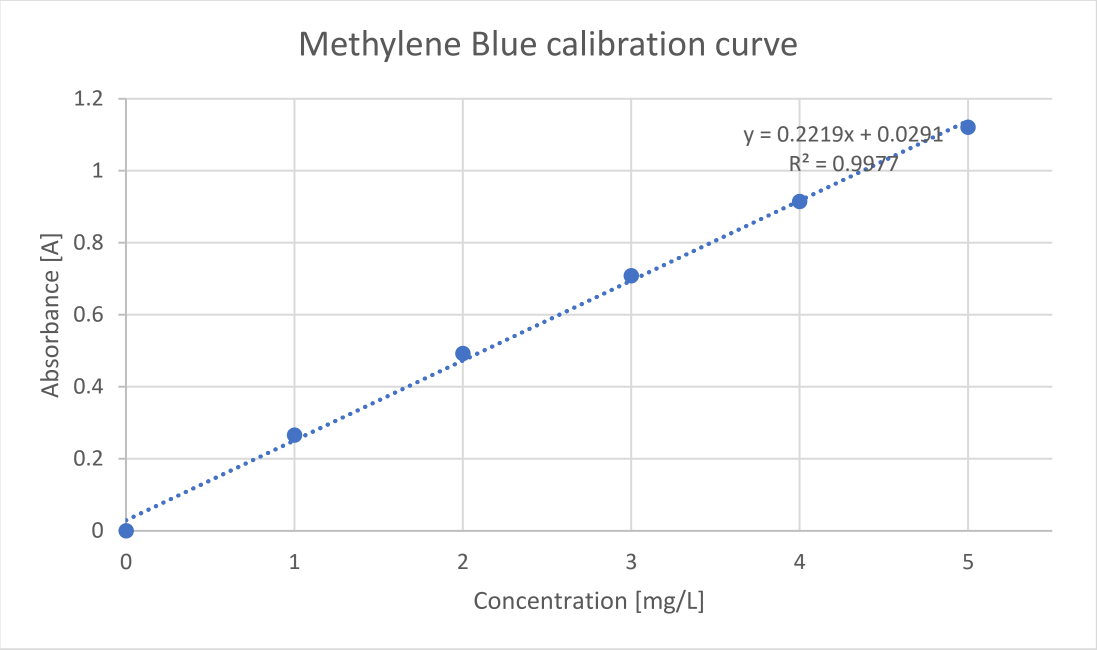
Initial MB concentration (mg/L)	Stock solution used	Stock solution Volume (mL)	Demiwater/Canal water Volume (mL)	Total solution Volume (mL)
20	1	20	480	500
200	2	50	450	500

A.2 Methylene Blue Calibration Curve

A.2.1. Calibration standards for MB

calibration standards							
	Concentration	mass MB	***Dilution***	***Demi***	***Stock***	***Absorption***	total volume
	(mg/L)	mg	***X***	***water***	***(uL)***	***(A)***	(L)
				(ml)			
Blanc	***0***	0	***-***	***10***	***-***	0	0.01
1	***1***	0.01	500	9.980	20	0.266	0.01
2	***2***	0.02	250	9.960	40	0.493	0.01
3	***3***	0.03	166.67	9.940	60	0.709	0.01
4	***4***	0.04	125	9.920	80	0.915	0.01
5	***5***	0.05	100	9.900	100	1.121	0.01

A.2.2. MB calibration curve



A.2.3. MB calibration curve parameters and equation

calibration curve	y = 0.2219x + 0.0291
intercept	0.029
slope	0.221

A.3 Adsorption experiments

A.3.1. DOPS carbon with demi water

Experiment 1

carbon Dose (g/L)	(g/0.5L)	Mass Ratio
0.05	0.025	0.4

time (hrs)	MB absorbance (A)	concentration (mg/L)	Dilution	MB concentration (mg/L)
0				20
0.5	0.854	3.717	5	18.583
1	1.342	5.915	3	17.746
1.5	1.331	5.866	3	17.597
2	1.324	5.834	3	17.503

2.5	1.301	5.731	3	17.192
3	1.28	5.636	3	16.908
19.5	1.242	5.465	3	16.394
20.5	1.248	5.492	3	16.475

removal efficiency (%)	**carbon loading qe (mg/L/g/l)**	Ce
18%	70.49433574	16.475

Experiment 2

carbon Dose (g/L)	(g/0.5L)	Mass Ratio
0.5	0.25	0.04

time (h)	**MB absorbance (A)**	**concentration (mg/L)**	**Dilution**	**MB concentration (mg/L)**
0				20
0.5	0.805	3.496	5	17.479
1	1.2	5.275	3	15.826
1.5	1.134	4.978	3	14.934
2	1.044	4.573	3	13.718
2.5	0.978	4.275	3	12.826
3	2.293	10.200	1	10.200
19.5	1.24	5.456	1	5.456
20.5	1.211	5.325	1	5.325
24	1.079	4.730	1	4.730

removal efficiency (%)	**carbon loading qe (mg/L/g/l)**	Ce
76%	30.53939238	4.730

carbon Dose (g/L)	(g/0.5L)	mass ratio (mgMB/mgGAC)
0.5044	0.2522	0.04

time (hours)	MB absorbance (A)	concentration (mg/L)	Dilution
0	0.905	3.946	5
1	0.703	3.036	5
2	0.618	2.653	5
3	0.565	2.414	5
5	0.48	2.031	5
6.5	0.439	1.847	5
22	1.133	4.974	1
23	1.12	4.915	1
25	1.076	4.717	1
30	0.998	4.365	1

Experiment 4

carbon Dose (g/L)	(g/0.5L)	Mass Ratio
5	2.5	0.004

time (hr)	MB absorbance (A)	concentration (mg/L)	Dilution	MB concentration (mg/L)
0			1	20
0.5	1.764	7.817	1	7.817
1	1.235	5.433	1	5.433
1.5	0.769	3.334	1	3.334
2	0.416	1.743	1	1.743
2.5	0.236	0.932	1	0.932
3	0.071	0.189	1	0.189
19.5	-0.015	0.000	1	0.000
20.5	-0.017	0.000	1	0.000
24	-0.003	0.000	1	0.000

removal efficiency (%)	carbon loading qe (mg/L/g/l)	Ce
100%	4	0.000

carbon Dose (g/L)	(g/0.5L)	mass ratio (mgMB/mgGAC)
5	2.5	0.004

time (hours)	MB absorbance (A)	concentration (mg/L)	Dilution	MB concentration (mg/L)
0				20.000
1	0.867	3.775	5	18.876
2	0.253	1.009	1	1.009
3	0.072	0.193	1	0.193
4	0.017	0.000	1	0.000
19	0.003	0.000	1	0.000
20	0.016	0.000	1	0.000
21	0	0.000	1	0.000

Experiment 3

carbon Dose (g/L)	(g/0.5L)	mass ratio (mgMB/mgGAC)
2	1	0.01

time (hours)	MB absorbance (A)	concentration (mg/L)	Dilution	MB concentration (mg/L)
0	0.874	3.807	5	19.033
1	0.493	2.090	5	10.450
2	1.088	4.771	1	4.771
3	0.703	3.036	1	3.036
4	0.333	1.369	1	1.369
5	0.181	0.684	1	0.684
7	0.048	0.085	1	0.085
21	0.001	0.000	1	0.000
22	0.001	0.000	1	0.000
26	0.001	0.000	1	0.000
31	0.001	0.000	1	0.000

removal efficiency (%)	carbon loading qe (mg/L/g/l)	Ce	
100%	9.516606591		0.000

carbon Dose (g/L)	(g/0.5L)	mass ratio (mgMB/mgGAC)

2	1	0.01

time (hours)	MB absorbance (A)	concentration (mg/L)	Dilution	MB concentration (mg/L)
0	0.779	3.379	5	16.893
1	0.518	2.203	5	11.013
2	1.794	7.952	1	7.952
3	0.971	4.244	1	4.244
4	0.926	4.041	1	4.041
5	0.392	1.635	1	1.635
6	0.241	0.955	1	0.955
21.5	0.001	0.000	1	0.000
23	0.001	0.000	1	0.000
25	0.003	0.000	1	0.000
30				

removal efficiency (%)	carbon loading qe (mg/L/g/l)	Ce
100%	8.446511329	0.000

Experiment 5

carbon Dose (g/L)	(g/0.5L)	mass ratio (mgMB/mgGAC)
2.016	1.008	0.1

time (hours)	Absorbance (A)	concentration (mg/L)	Dilution	MB concentration (mg/L)
0	0.855	3.721	50	186.052
1	0.705	3.045	50	152.259
4	0.614	2.635	50	131.758
6	0.579	2.477	50	123.874
20	0.535	2.279	50	113.961
24.5	0.54	2.302	50	115.088
30	0.528	2.248	50	112.384
44	0.53	2.257	50	112.835
48	0.512	2.176	50	108.780
51	0.51	2.167	50	108.329

removal efficiency (%)	carbon loading qe (mg/L/g/l)	Ce
42%	38.55293	108.329

A.3.2. DOPS carbon with canal water

Experiment 4

carbon Dose (g/L)	(g/0.5L)	mass ratio (mgMB/mgGAC)
5	2.5	0.004

time (hours)	Absorbance MB (A)	Absorbance NOM (A)	concentration (mg/L)	Dilution
0	0.83	0.206	3.608	5
1	0.299	0.08	1.216	5
2	0.728	0.266	3.149	1
3	0.338	0.169	1.392	1
5	0.073	0.099	0.198	1
6	0.03	0.081	0.004	1

MB removal (%)	carbon loading qe (mg/L/g/l)	Ce
100%	3.607621009	0.004
NOM removal		
61%		

A.3.3. Norit carbon with demi water

Experiment 3

carbon Dose (g/L)	(g/0.5L)	mass ratio (mgMB/mgGAC)
2	1	0.01

time (hours)	MB absorbance (A)	concentration (mg/L)	Dilution	MB concentration (mg/L)
0	0.742	3.212	6	19.271
1	0.629	2.703	5	13.514
2	1.827	8.101	1	8.101
3	1.48	6.537	1	6.537
4	1.033	4.523	1	4.523
5	0.764	3.311	1	3.311
7	0.405	1.693	1	1.693
21	0.004	0.000	1	0.000
22	0.002	0.000	1	0.000
26	0.002	0.000	1	0.000
31	0.002	0.000	1	0.000

MB removal (%)	carbon loading qe (mg/L/g/l)	Ce	
100%	9.635684861		0.000

Experiment 2

carbon Dose (g/L)	(g/0.5L)	mass ratio (mgMB/mgGAC)
0.503	0.2515	0.04

time (hours)	Absorbance (A)	concentration (mg/L)	Dilution	MB concentration (mg/L)
0	0.906	3.951	5	19.754
1	0.782	3.392	5	16.961
2	0.715	3.090	5	15.451
3	0.671	2.892	5	14.460
5	0.585	2.505	5	12.523
6.5	0.538	2.293	5	11.464
22	1.091	4.784	1	4.784
23	1.044	4.573	1	4.573
25	0.95	4.149	1	4.149
30	0.746	3.230	1	3.230

MB removal (%)	carbon loading qe (mg/L/g/l)	Ce	
84%	32.85129593		3.230

Experiment 4

carbon Dose (g/L)	(g/0.5L)	mass ratio (mgMB/mgGAC)
5	2.5	0.004

time (hours)	Absorbance (A)	concentration (mg/L)	Dilution	MB concentration (mg/L)
0	0.956	4.176	5	20.881
1	0.36	1.491	5	7.454
2	0.73	3.158	1	3.158
3	0.398	1.662	1	1.662
4	0.189	0.720	1	0.720

MB removal (%)	carbon loading qe (mg/L/g/l)	Ce	
97%	4.032055		0.720

Experiment 5

Norit (GAC 830 P.)

22/02/2023

carbon Dose (g/L)	(g/0.5L)	mass ratio (mgMB/mgGAC)
2.006	1.003	0.1

time (hours)	Absorbance (A)	concentration (mg/L)	Dilution	MB concentration (mg/L)
0	0.86	3.744	50	187.178
1	0.736	3.185	50	159.243
4	0.602	2.581	50	129.055
6	0.556	2.374	50	118.692
20	0.373	1.549	50	77.465
24.5	0.337	1.387	50	69.355
30	0.301	1.225	50	61.245
44	0.226	0.887	50	44.349
48	0.207	0.801	50	40.068
51	0.188	0.716	50	35.788

MB removal (%)	carbon loading qe (mg/L/g/l)	Ce
81%	75.46875	35.788

A.3.4. Norit carbon with canal water

Experiment 4

carbon Dose (g/L)	(g/0.5L)	mass ratio (mgMB/mgGAC)
5	2.5	0.004

time (hours)	Absorbance MB (A)	Absorbance NOM (A)	concentration (mg/L)	Dilution
0	0.828	0.204	3.599	5
1	0.361	0.108	1.495	5
2	0.916	0.388	3.996	1
3	0.455	0.279	1.919	1
5	0.104	0.191	0.337	1
6	0.047	0.167	0.080	1

MB removal (%)	carbon loading qe (mg/L/g/l)	Ce
100%	3.583290422	0.080

NOM removal
18%

A.3.5. Precursor material

Experiment 1

carbon Dose (g/L)	(g/0.5L)
0.05	0.025

time (hrs)	MB absorbance (A)	concentration (mg/L)	Dilution	MB concentration (mg/L)
0	0.906	3.951	5	19.754
1	0.858	3.735	5	18.673
2	0.846	3.680	5	18.402
3	0.837	3.640	5	18.200
4	0.84	3.653	5	18.267
6	0.816	3.545	5	17.727
7.5	0.816	3.545	5	17.727
23	0.75	3.248	5	16.240
26	0.743	3.216	5	16.082
29	0.716	3.095	5	15.474

removal efficiency (%)	carbon loading qe (mg/L/g/l)	Ce
23%	85.60762101	15.474

Experiment 2

carbon Dose (g/L)	(g/0.5L)
0.5	0.25

time (h)	MB absorbance (A)	concentration (mg/L)	Dilution	MB concentration (mg/L)
0	0.886	3.861	5	19.304
1	0.677	2.919	5	14.595
2	0.577	2.468	5	12.342

3	0.519	2.207	5	11.036
4	0.484	2.049	5	10.247
6	0.39	1.626	5	8.130
7.5	0.347	1.432	5	7.161
23	0.866	3.771	1	3.771
26	0.824	3.581	1	3.581
29	0.732	3.167	1	3.167

removal efficiency (%)	carbon loading qe (mg/L/g/l)	Ce
84%	32.27342945	3.167

Experiment 3

carbon Dose (g/L)	(g/0.5L)
2	1

time (hr)	MB absorbance (A)	concentration (mg/L)	Dilution	MB concentration (mg/L)
0	0.898	3.915	5	19.574
1	0.438	1.842	5	9.211
2	1.286	5.663	1	5.663
3	1.035	4.532	1	4.532
4	0.888	3.870	1	3.870
6	0.619	2.658	1	2.658
7.5	0.541	2.306	1	2.306
23	0.299	1.216	1	1.216
26	0.284	1.148	1	1.148
29	0.241	0.955	1	0.955

removal efficiency (%)	carbon loading qe (mg/L/g/l)	Ce
95%	9.309668	0.955

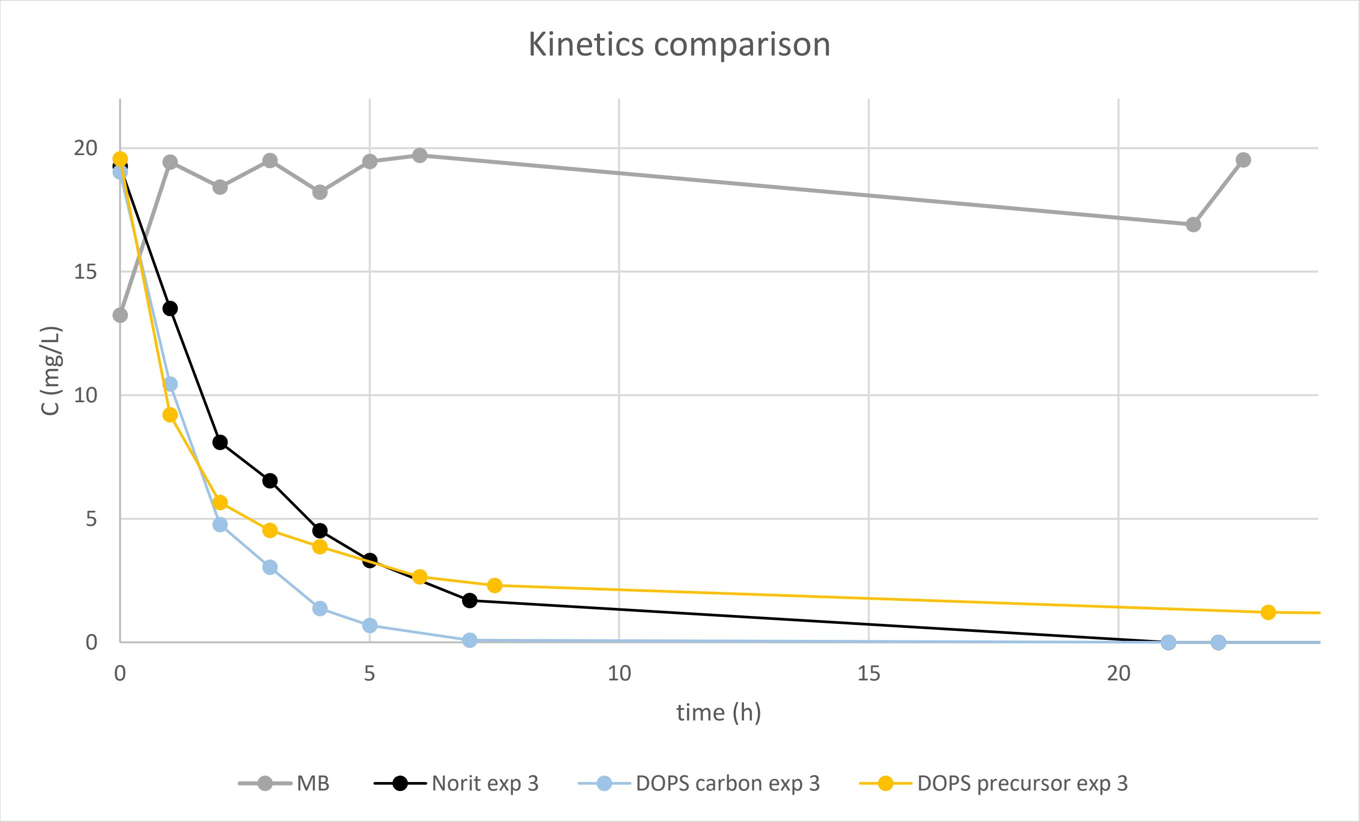
A.4 Adsorption experiment replicates

experiment number	values	DOPS carbon

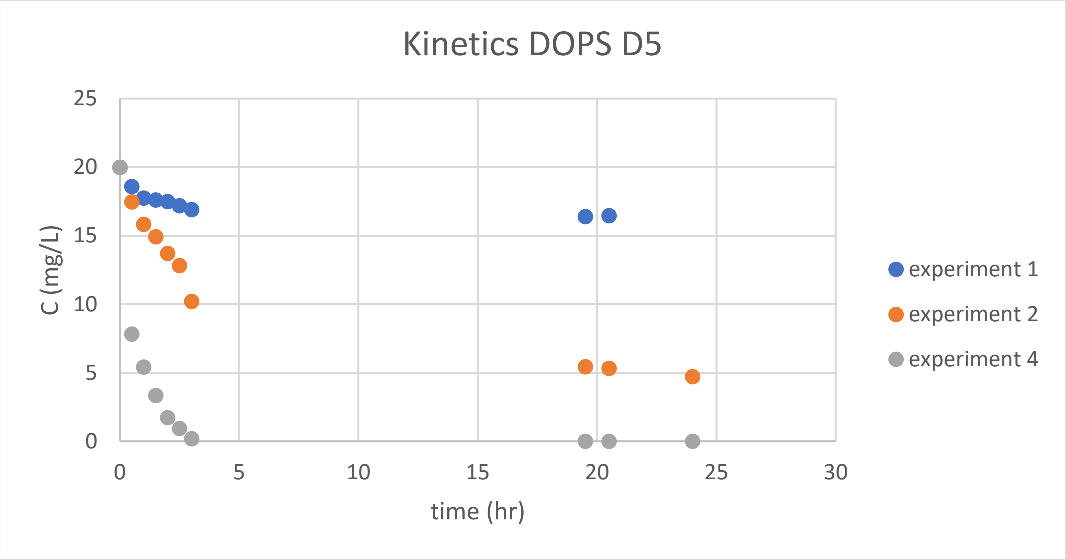
2	actual C0	20
	Ce	4.730
	qe	30.539
	ηremoval	76%
3	actual C0	20
	Ce	0
	qe	4
	ηremoval	100%
3	actual C0	16.893
	Ce	0.0
	qe	8.447
	ηremoval	100%

A.5 Kinetics

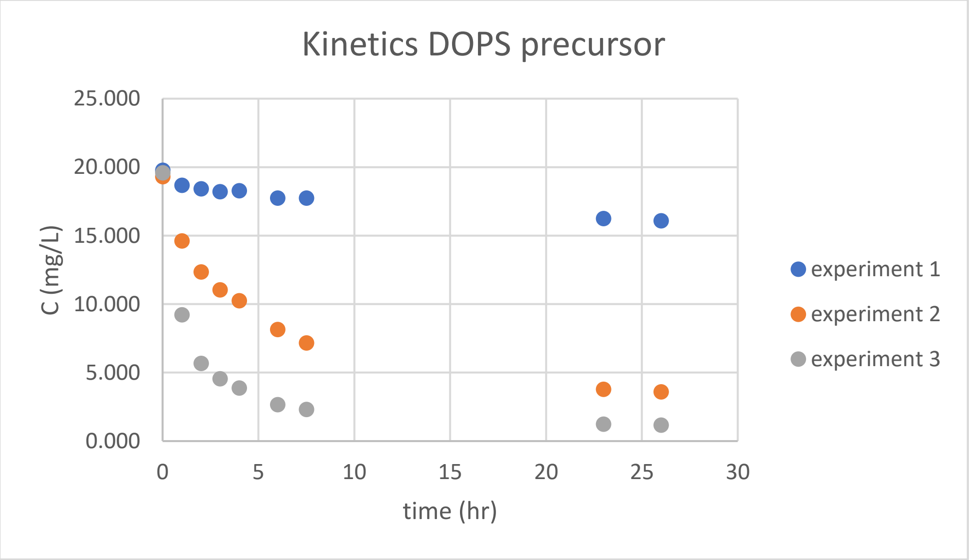
A.5.1. Methylene blue and carbons



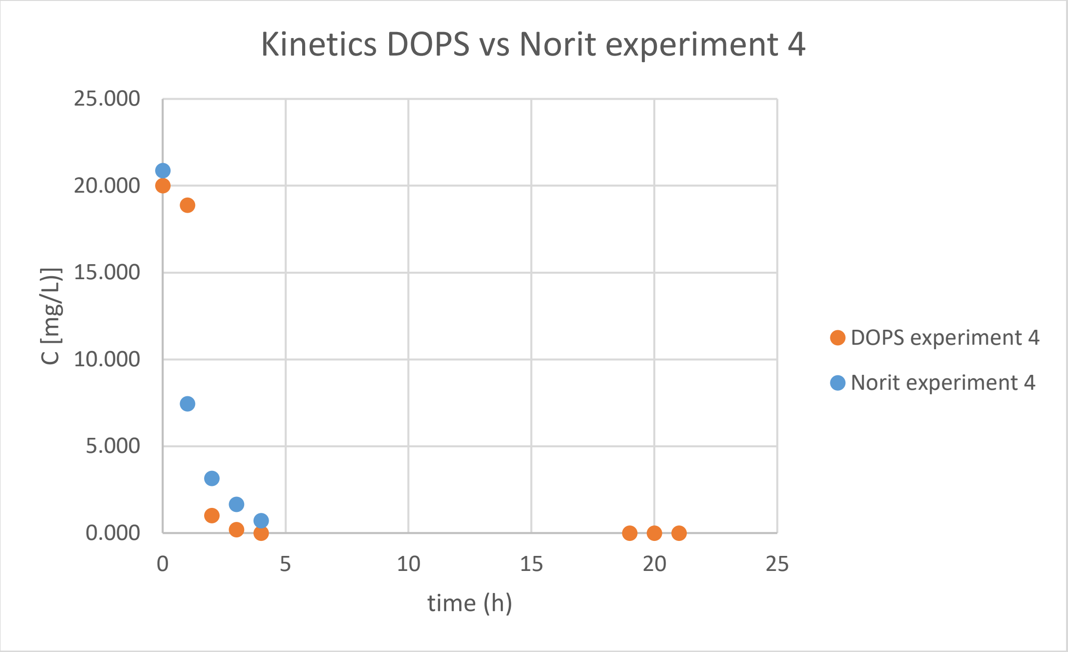
A.5.2. DOPS carbon

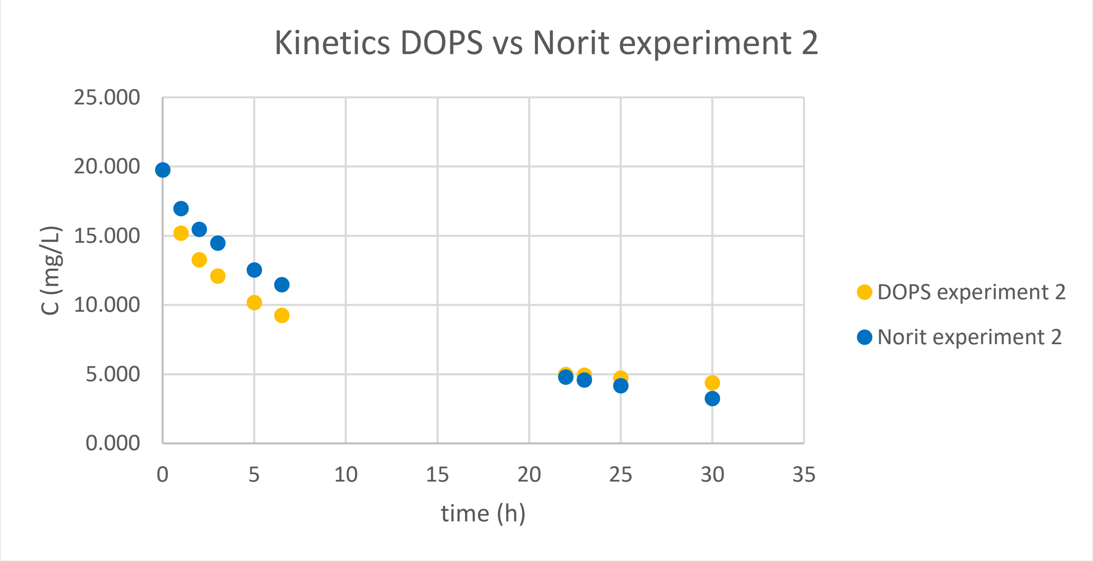


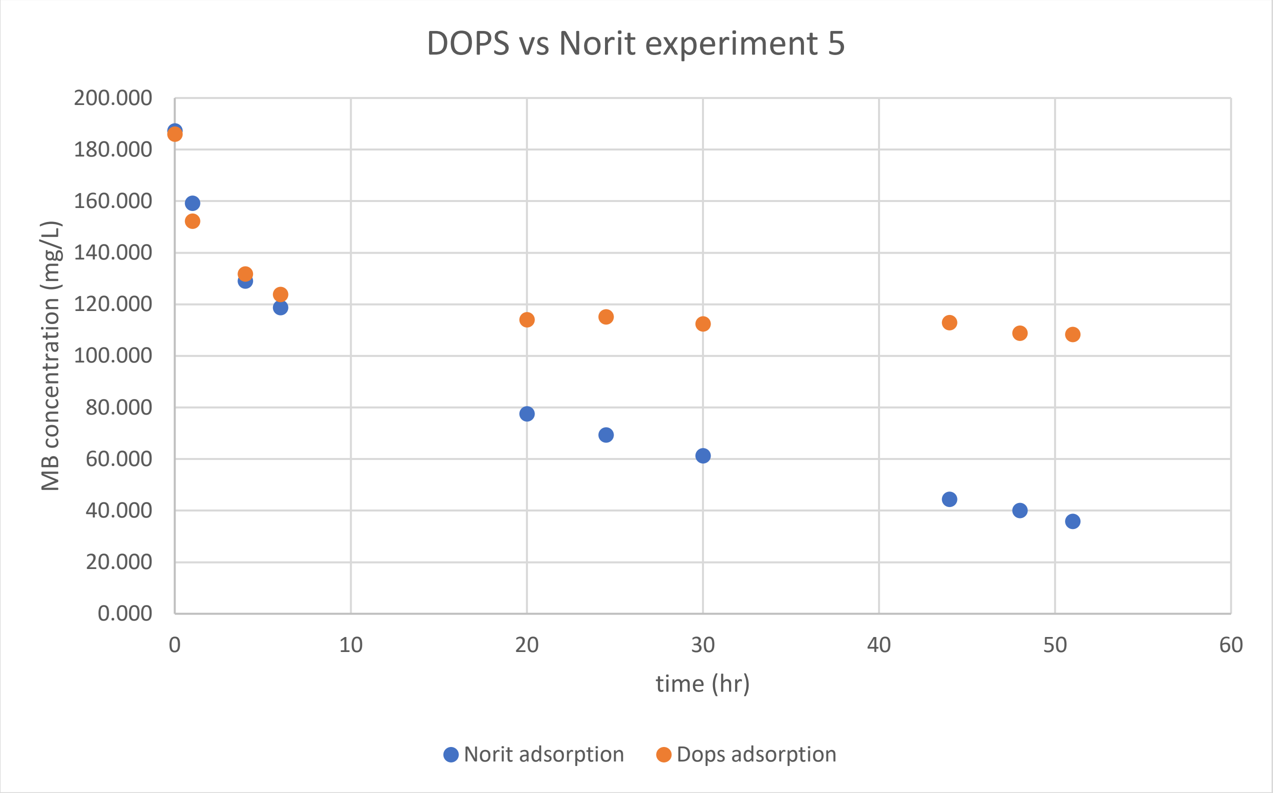
A.5.3. Precursor



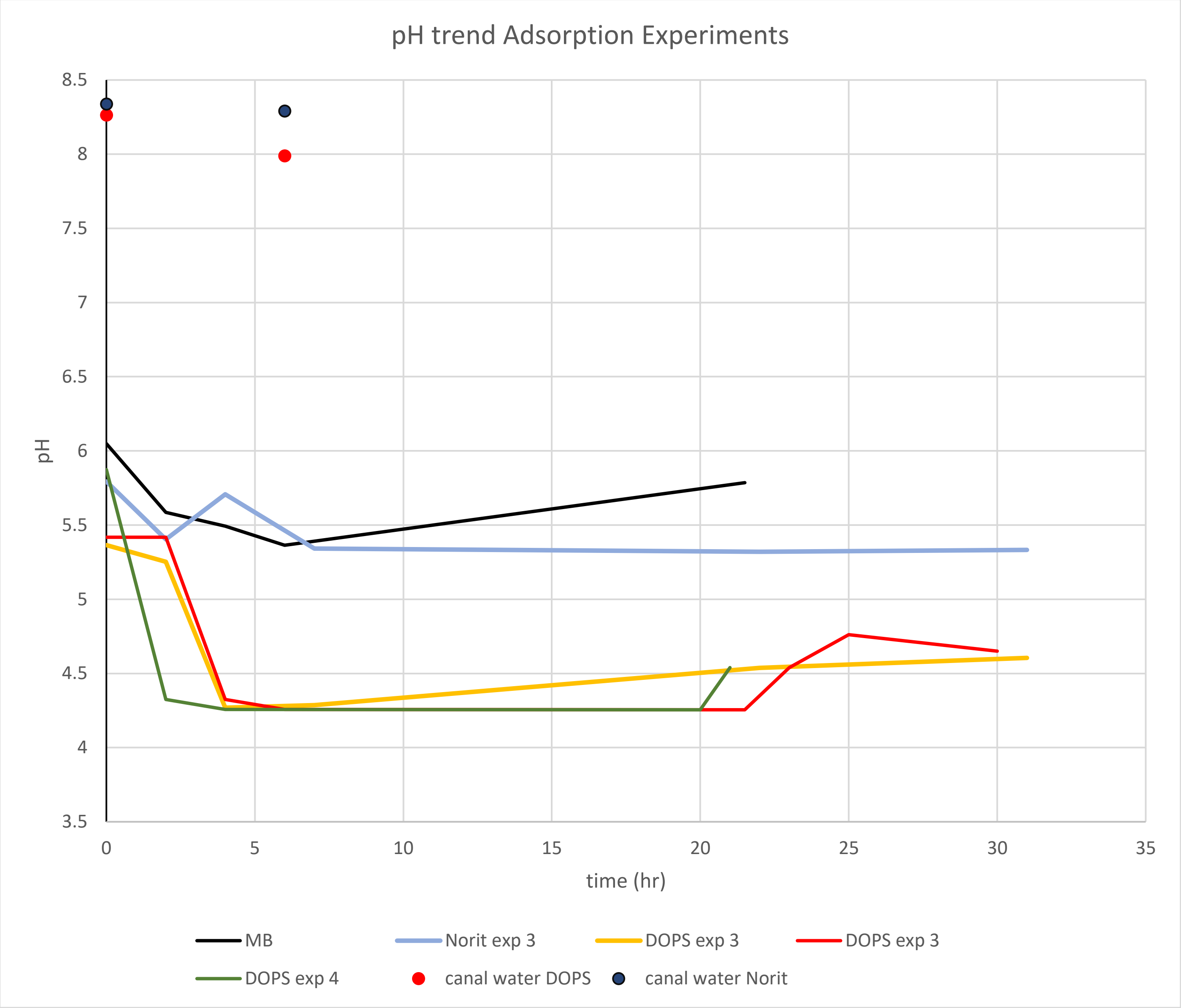
A.5.4. DOPS vs Norit






DOPS vs Norit experiment 5
MB concentration (mg/L)
200.000
180.000
160.000
140.000
120.000
100.000
80.000
60.000
40.000
20.000
0.000
0
10
20
30
40
50
60
time (hr)
● Norit adsorption
● Dops adsorption

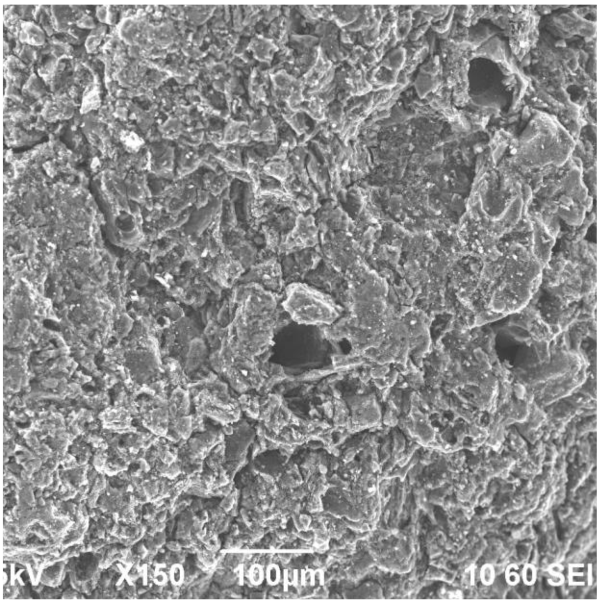
A.6 pH trend


pH trend Adsorption Experiments
pH
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
0
5
10
15
20
25
30
35
time (hr)
MB
Norit exp 3
DOPS exp 3
DOPS exp 3
DOPS exp 4
canal water DOPS
canal water Norit

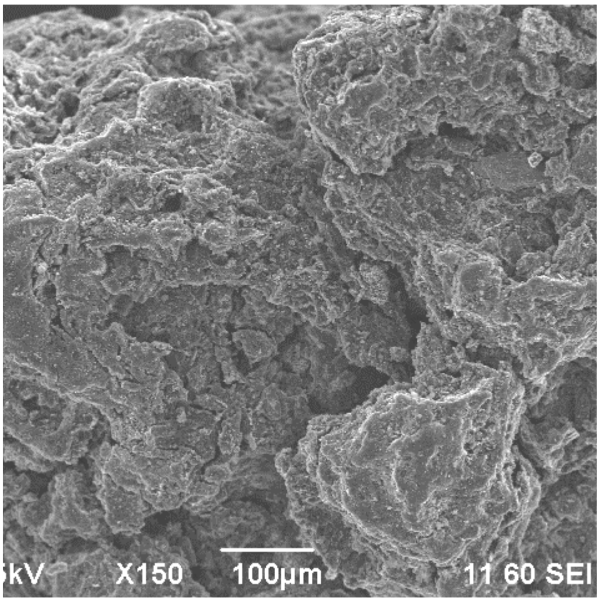
A.7 SEM images

A.7.1. External Surface

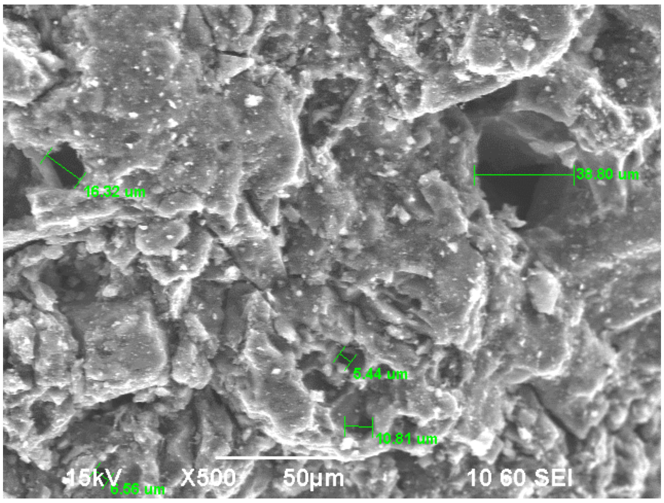
Norit x150



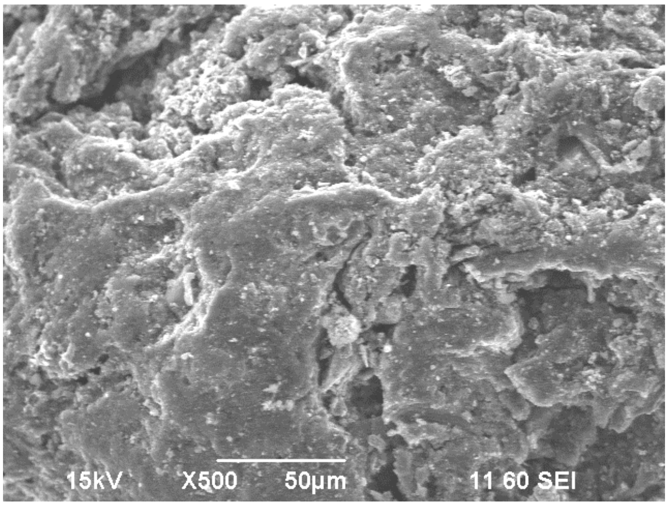
DOPS x150



A.7.2. Cut – surface



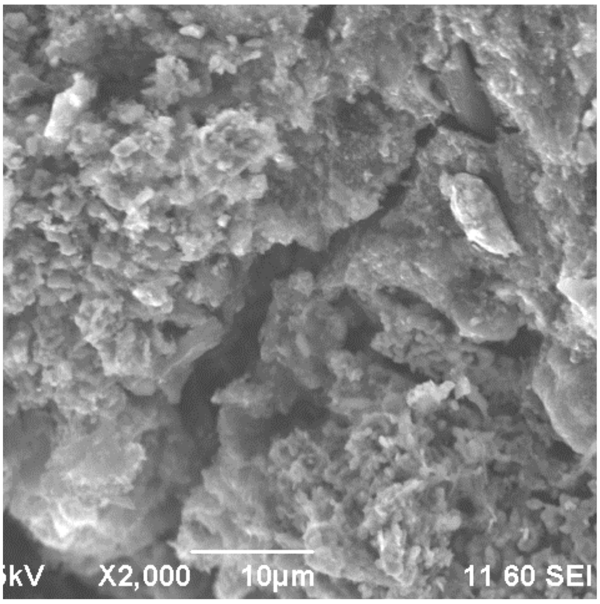
Norit x500



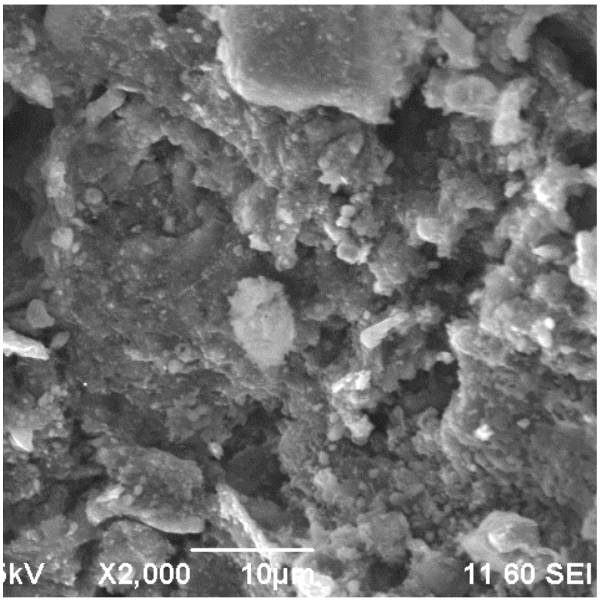
DOPS x500

A.7.3. Cut - surface

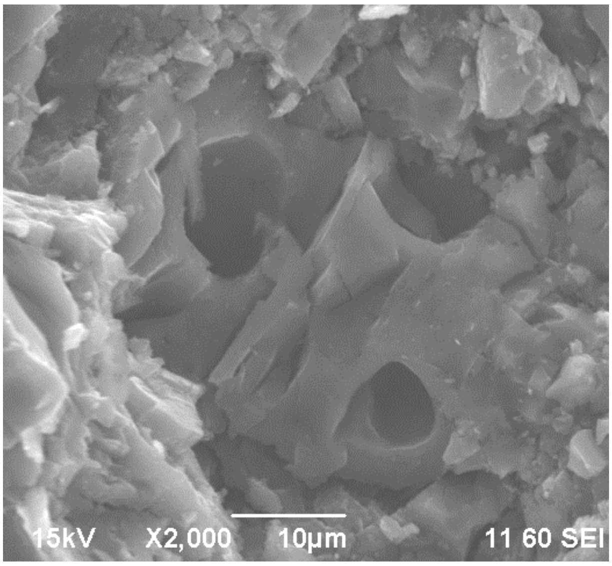
DOPS x2000



DOPS x2000

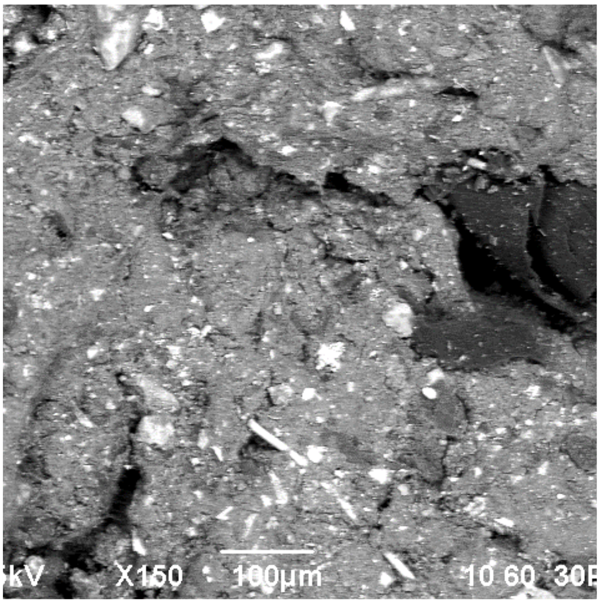


Norit x2000

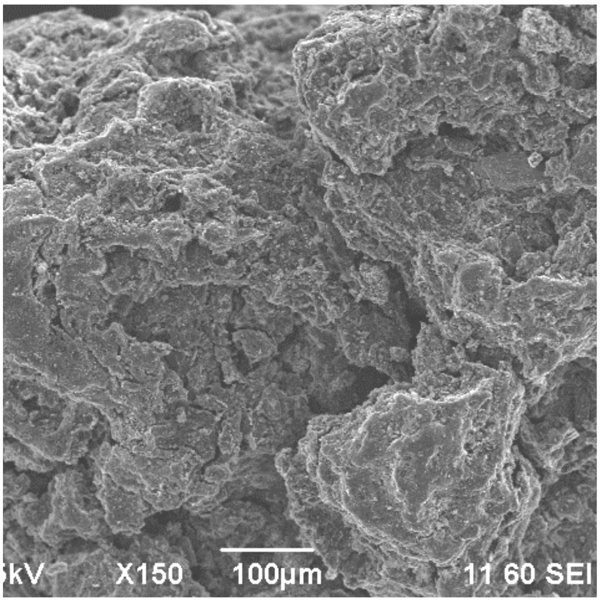


A.7.4. External surface

Precursor x150

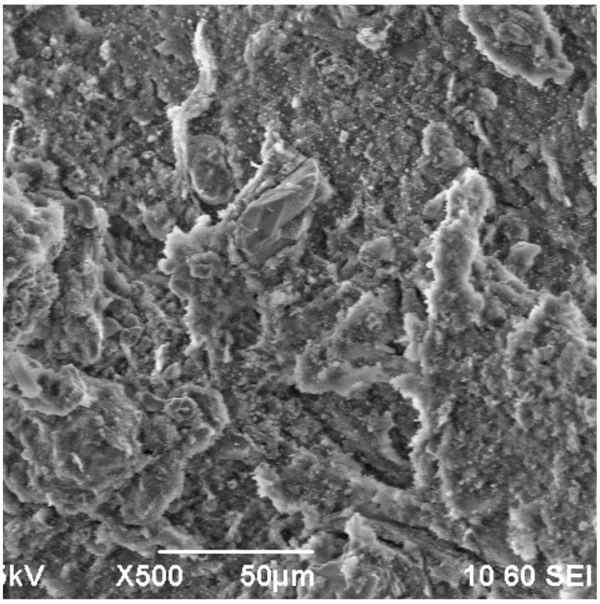


DOPS x150

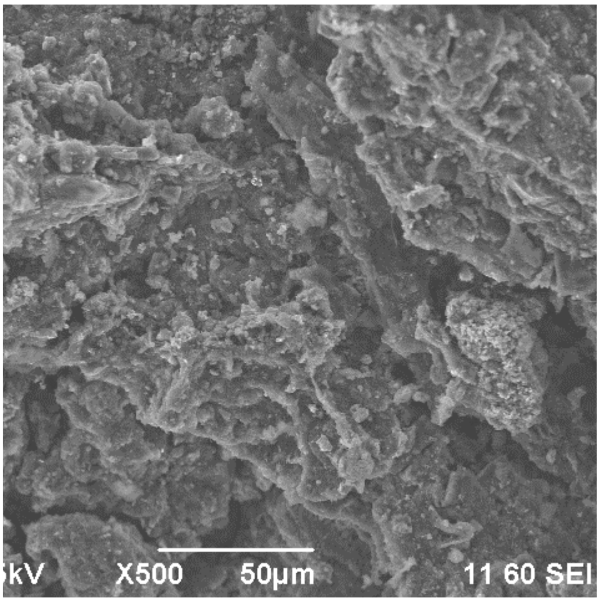


A.7.5. Sacrificial Sludge vs DOPS carbon

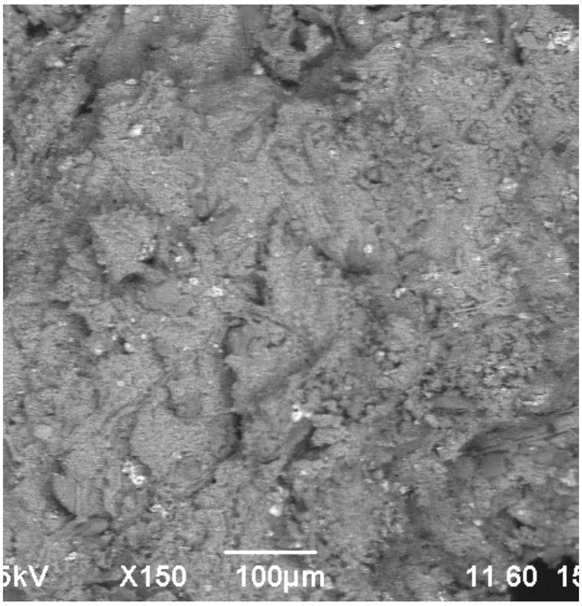
Sacrificial sludge x500



DOPS x150

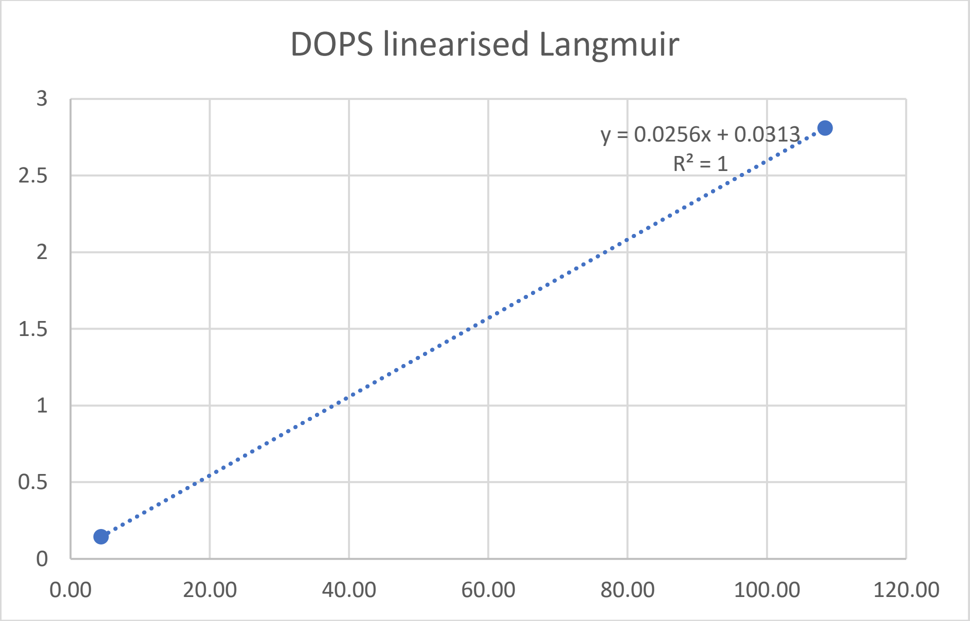


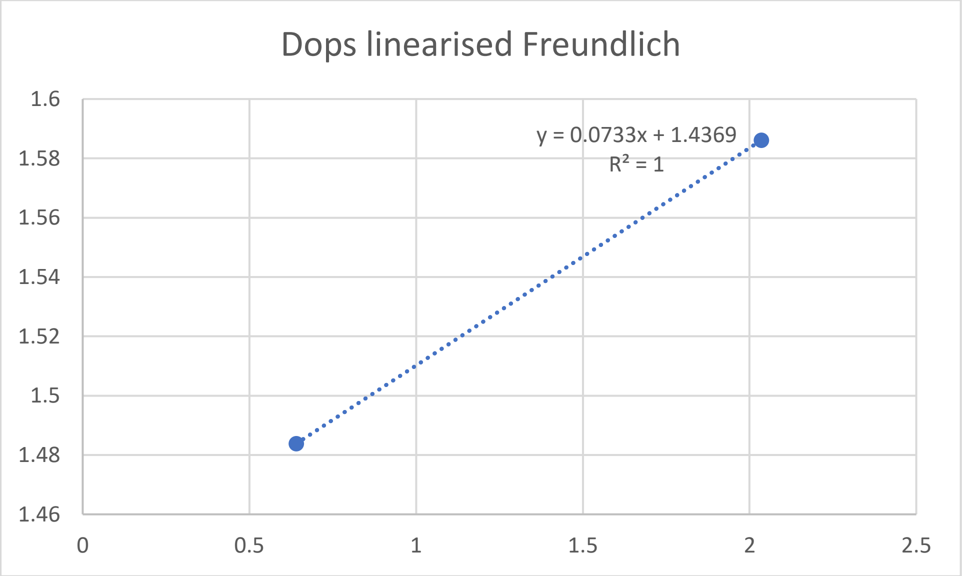
Sacrificial sludge x150



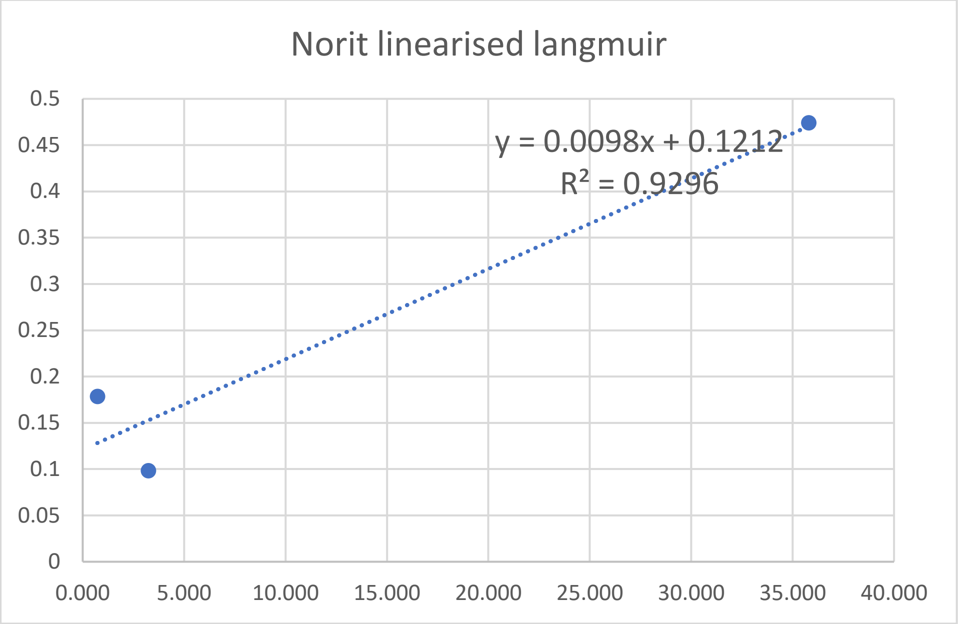
A.8 Isotherms

A.8.1. DOPS linearization

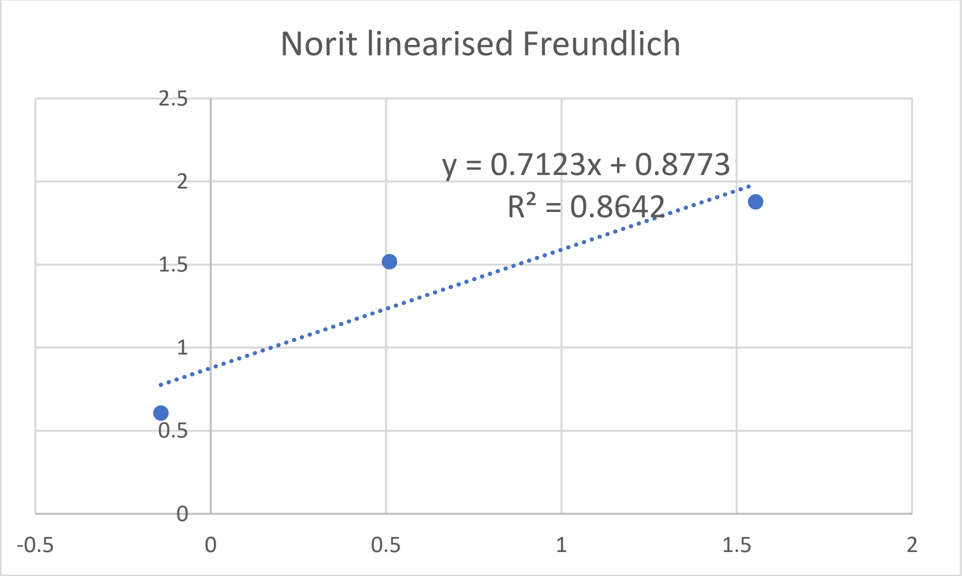




A.8.2. Norit linearization

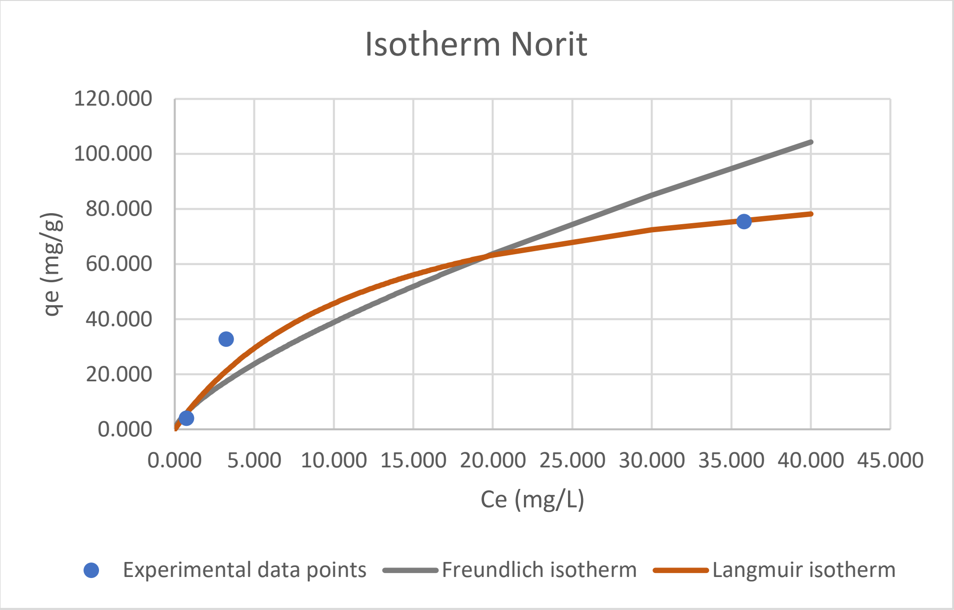


qmax	b
102.4949	0.080532

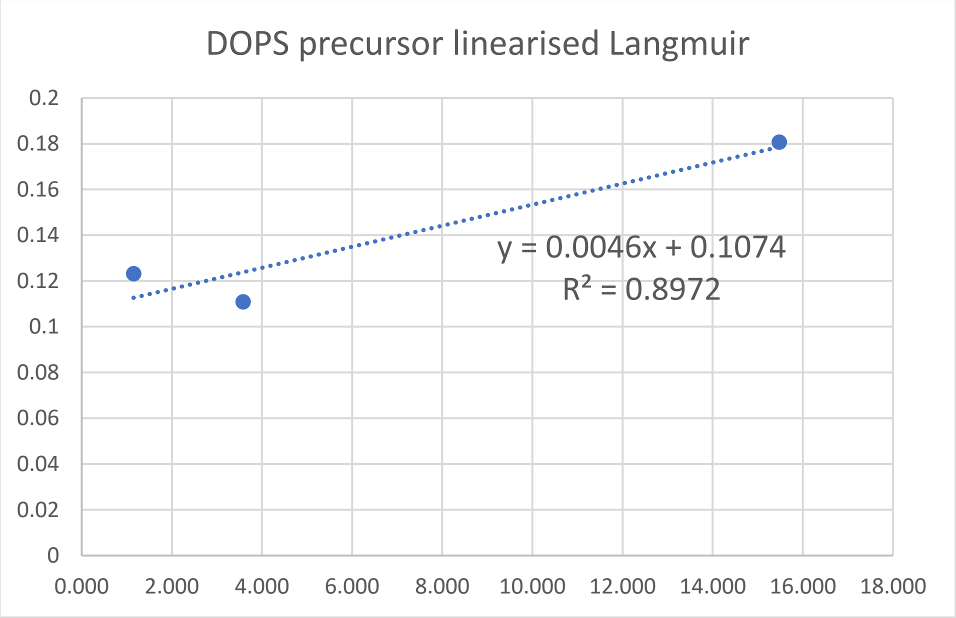


kf	n
7.539213	0.712276

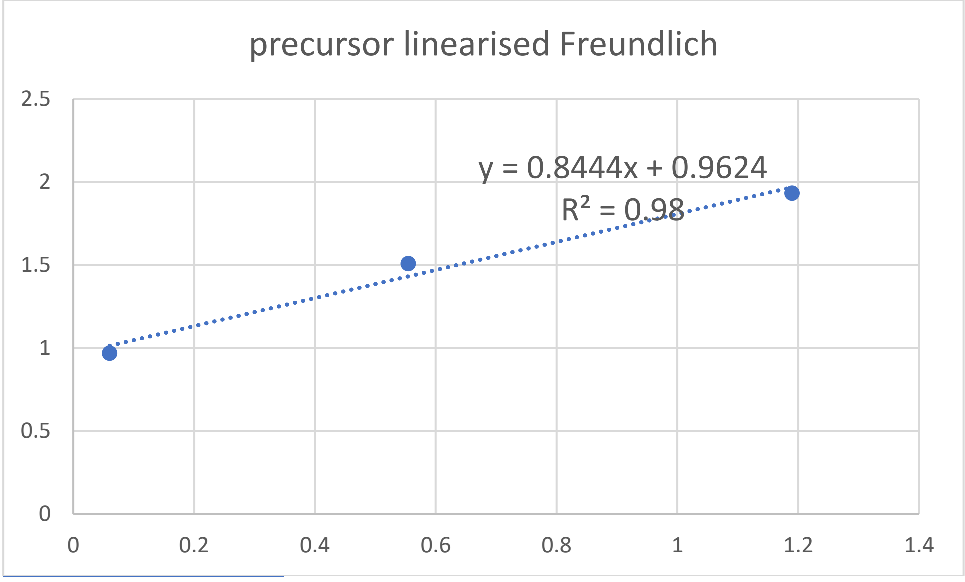
A.8.3. Norit isotherm



A.8.4. Precursor linearization

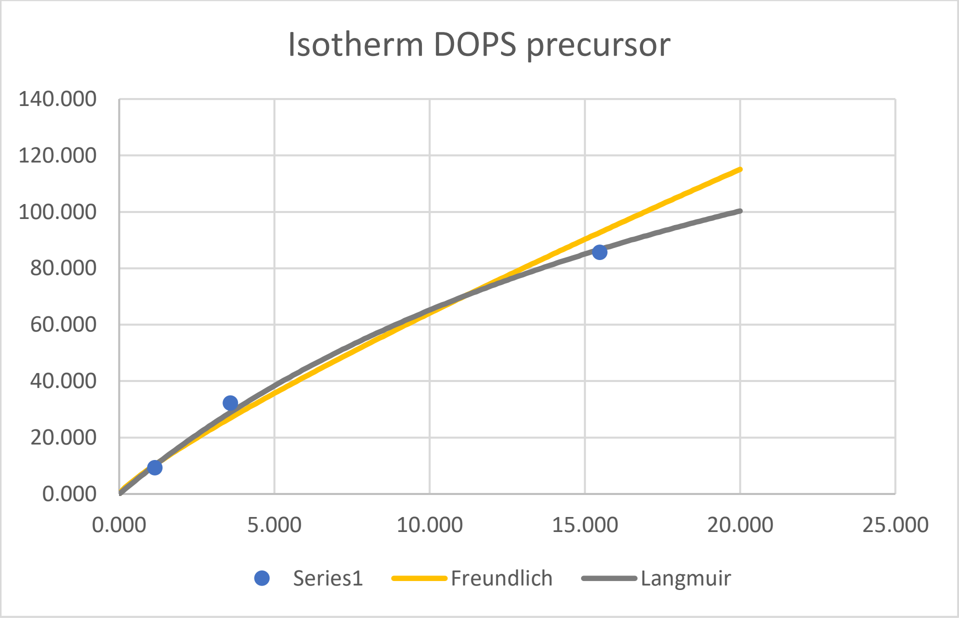


qmax	b
217.3453	0.042851



kf	**n**
9.171594	0.844352

A.8.5. Precursor isotherm



A.9 Leaching tests

A.9.1 Expected concentrations for experiments on DOPS carbon

na pyrolosis	**g**	**kg**	**L (adsorption experiment, pH 4.5)**
carbon	1	0.001	
Adsorption Solution Volume			0.5

	mg/kg in carbon	mg	mg/L (max potential in water)
As	11.7	0.0117	0.0234
Cr	121.9	0.1219	0.2438
Cu	497.9	0.4979	0.9958
Zn	1316	1.316	2.632
Ni	99.9	0.0999	0.1998
Pb	8.74	0.00874	0.01748

A.9.2 Expected concentrations for precursor material

voor pyrolysis	**g**	**kg**	**L (adsorption experiment, pH 4.5)**
carbon	1	0.001	
Adsorption Solution Volume			0.5

	mg/kg in carbon	mg	mg/L (max potential in water)
As	13.2	0.0132	0.0264
Cr	115.7	0.1157	0.2314
Cu	481	0.481	0.962
Zn	2283	2.283	4.566
Ni	96.1	0.0961	0.1922
Pb	109.1	0.1091	0.2182

A.9.3 Leaching tests: precursor material ICP-OES results at different wavelengths

experiment n	**soaking time (hr)**	As (188.980 nm) ppm	**As (193.696 nm) ppm**	**Cr (267.716 nm) ppm**	Cu (327.395 nm) ppm	Cu (219.227 nm) ppm	Cu (324.754 nm) ppm	Cu (224.700 nm) ppm	**Cu Average ppm**
1	51	0.002	0.004	-0.001	0.045	0.047	0.05	0.048	0.05
2	51	0	0.001	-0.001	0.036	0.037	0.04	0.04	0.04
3	51	0	0.002	-0.001	0.011	0.011	0.01	0.013	0.01

Ni (231.604 nm) ppm	Ni (216.555 nm) ppm	Ni (221.648 nm) ppm	**Ni Average ppm**	**Pb (220.353 nm) ppm**	Zn (213.857 nm) ppm	Zn (202.548 nm) ppm	Zn (206.200 nm) ppm	Zn (334.502 nm) ppm	**Zn Average ppm**
0.006	0.007	0.006	0.01	0.002	0.017	0.017	0.016	0.01	0.02
0.001	0.002	0.001	0	0.003	0.007	0.008	0.007	0	0.01
-0.001	0	0		0.003	0.008	0.008	0.008	0.01	0.01

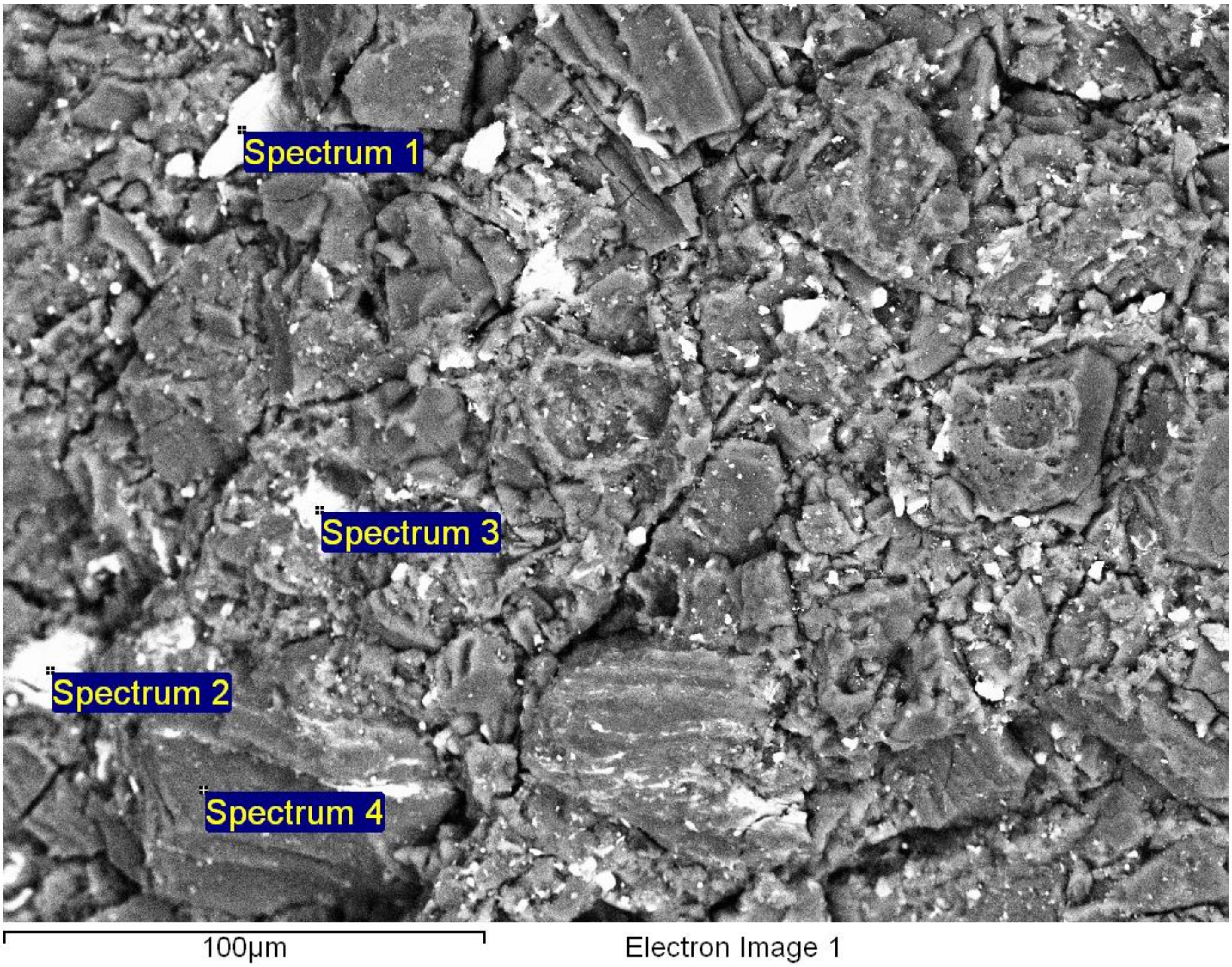
EDX analysis results

Project 1

2/23/2023 9:43:47 AM

Project: Project 1
Owner: INCA
Site: Site of Interest 1

Sample: Commercial Norit – external surface
Type: Default
ID:



Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	O	Na	Mg	Al	Si	S	K	Ca	Ti	Fe	Total
Spectrum 1	Yes	13.18	54.20	0.61	0.61	10.59	14.98	0.76	2.35			2.73	100.00
Spectrum 2	Yes	35.89	23.45	0.20		10.81	24.05	0.28	3.20		0.50	1.63	100.00
Spectrum 3	Yes	19.75	45.55	0.44	0.44	11.13	17.09	0.28	2.47	0.32		2.52	100.00
Spectrum 4	Yes	93.06	6.22					0.73					100.00
Max.		93.06	54.20	0.61	0.61	11.13	24.05	0.76	3.20	0.32	0.50	2.73	
Min.		13.18	6.22	0.20	0.44	10.59	14.98	0.28	2.35	0.32	0.50	1.63	

All results in weight%

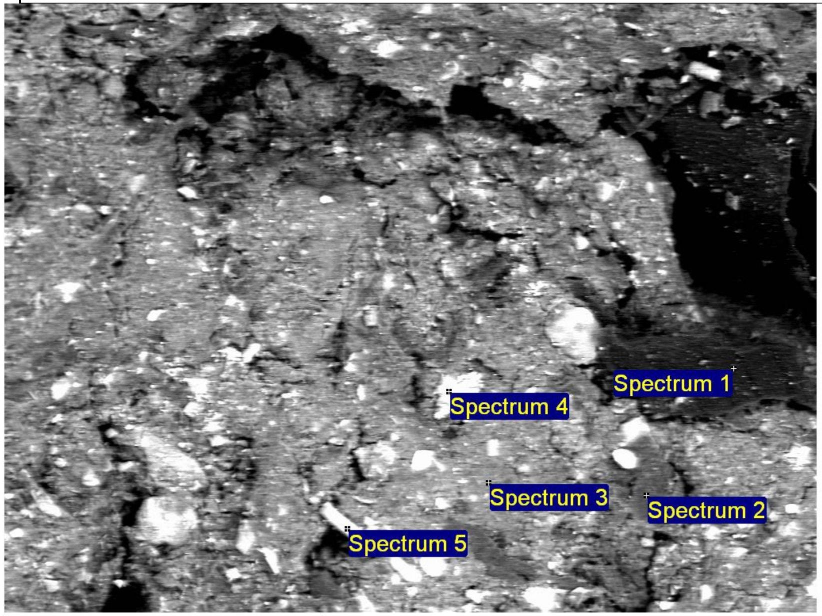
Project 1

2/23/2023 9:44:08 AM

Project: Project 1
Owner: INCA
Site: Site of Interest 3

Sample:
Precursor material – external surface

Comment:



Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	O	Na	Mg	Al	Si	P	S	K	Ca	Ti	Fe	Total
Spectrum 1	Yes	50.81	31.28	0.37		2.30	3.34	1.27	2.37	0.56	2.38		5.33	100.00
Spectrum 2	Yes	45.70	40.95		0.46	2.68	2.62	1.51	1.43	0.39	1.99		2.26	100.00
Spectrum 3	Yes	32.45	34.30		0.58	4.16	6.05	5.04	2.75	0.50	5.72		8.46	100.00
Spectrum 4	Yes	16.65	55.52	0.21	1.09	0.92	0.67	9.26	0.16		1.04		14.47	100.00
Spectrum 5	Yes	15.36	44.09	1.19	2.45	6.95	14.49	1.16	0.53	0.33	9.28	0.48	3.70	100.00
Max.		50.81	55.52	1.19	2.45	6.95	14.49	9.26	2.75	0.56	9.28	0.48	14.47	
Min.		15.36	31.28	0.21	0.46	0.92	0.67	1.16	0.16	0.33	1.04	0.48	2.26	

All results in weight%

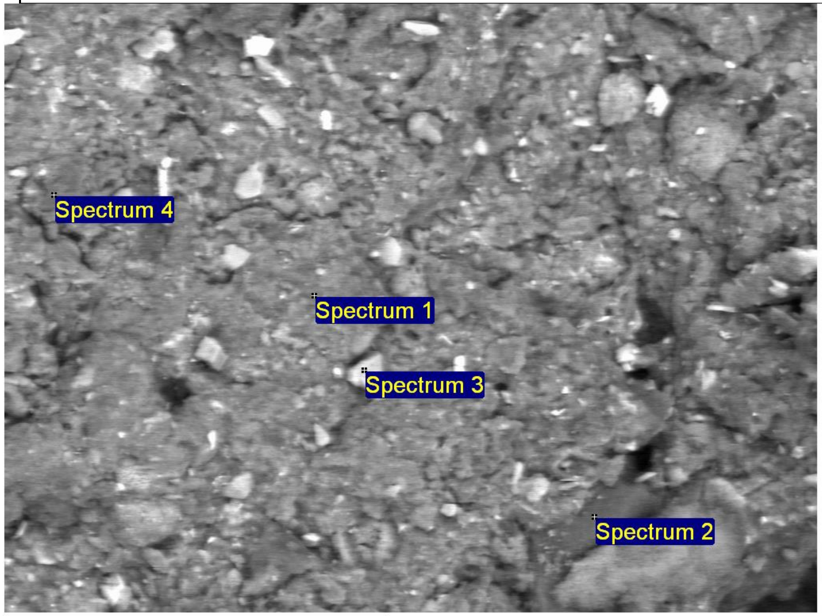
Project 1

2/23/2023 9:44:18 AM

Project: Project 1
Owner: INCA
Site: Site of Interest 1

Sample:
Precursor material – cut surface

Comment:



Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	O	Na	Mg	Al	Si	P	S	K	Ca	Fe	Total
Spectrum 1	Yes	32.07	48.00	0.19	0.33	3.76	8.71	1.99	1.16	0.28	1.60	1.90	100.00
Spectrum 2	Yes	47.35	41.22	0.15	0.40	3.05	2.21	1.37	0.72		1.52	2.00	100.00
Spectrum 3	Yes	28.22	36.69	5.04		9.24	14.86	0.97	0.65	1.46	1.26	1.60	100.00
Spectrum 4	Yes	39.88	33.21		0.64	4.83	5.89	2.80	2.63	1.19	1.97	6.96	100.00
Max.		47.35	48.00	5.04	0.64	9.24	14.86	2.80	2.63	1.46	1.97	6.96	
Min.		28.22	33.21	0.15	0.33	3.05	2.21	0.97	0.65	0.28	1.26	1.60	

All results in weight%

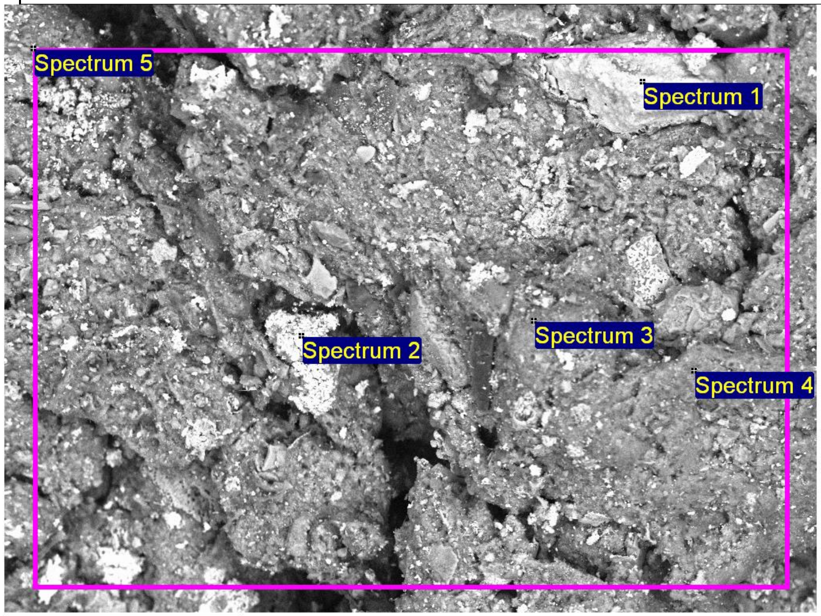
Project 1

2/23/2023 9:44:38 AM

Project: Project 1
Owner: INCA
Site: Site of Interest 1

Sample:
DOPS DCI carbon – external surface

Comment:



Processing option : All elements analysed (Normalised)

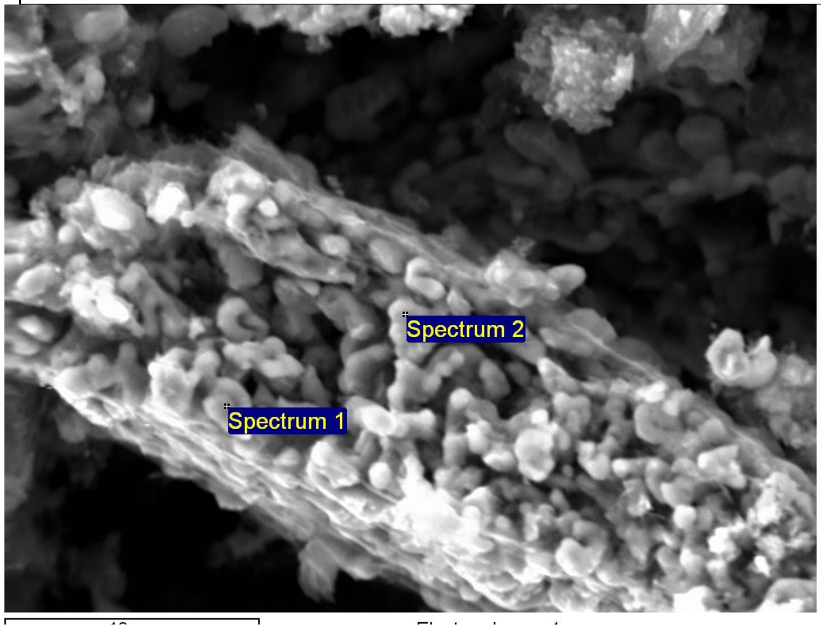
Spectrum	In stats.	C	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	Total
Spectrum 1	Yes	3.42	38.47		0.33	0.52		18.04	1.34	2.36		34.52		1.01	100.00
Spectrum 2	Yes	7.90	13.03			0.82	0.66	11.19	1.82			1.10		63.49	100.00
Spectrum 3	Yes	30.33	39.61	0.50	2.11	13.83	3.50	3.04	1.23		0.41	2.25	0.19	3.00	100.00
Spectrum 4	Yes	13.09	22.11	0.36	3.31	25.66	7.86	6.25	2.56	0.66	1.63	11.57	0.88	4.08	100.00
Spectrum 5	Yes	29.07	33.89	0.63	1.00	6.79	7.95	4.91	1.39		0.66	7.49		6.23	100.00
Max.		30.33	39.61	0.63	3.31	25.66	7.95	18.04	2.56	2.36	1.63	34.52	0.88	63.49	
Min.		3.42	13.03	0.36	0.33	0.52	0.66	3.04	1.23	0.66	0.41	1.10	0.19	1.01	

All results in weight%

Project: Project 1
Owner: INCA
Site: Site of Interest 1

Sample:
DOPS DCI carbon – cut surface mineral

Comment:



Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	F	Mg	Al	Si	P	Ca	Fe	Total
Spectrum 1	Yes	18.10	2.71		0.18	0.45	27.62	0.28	50.67	100.00
Spectrum 2	Yes	21.24	2.71	0.27	0.23	0.17	29.45	0.33	45.59	100.00
Max.		21.24	2.71	0.27	0.23	0.45	29.45	0.33	50.67	
Min.		18.10	2.71	0.27	0.18	0.17	27.62	0.28	45.59	

All results in weight%

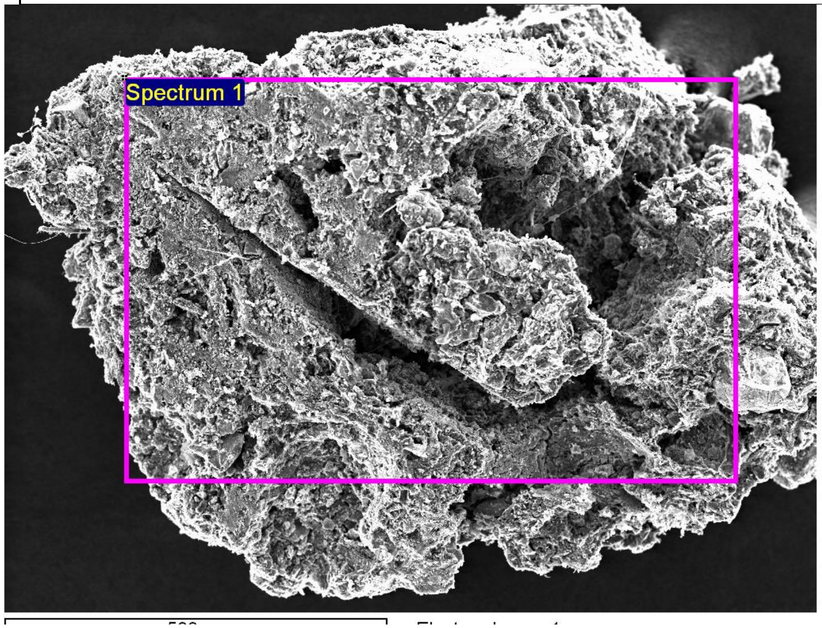
Project 1

2/23/2023 9:45:09 AM

Project: Project 1
Owner: INCA
Site: Site of Interest 2

Sample:
DOPS DCI carbon – cut surface

Comment:



Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Fe	Total
Spectrum 1	Yes	31.88	32.73	0.47	0.56	5.44	8.85	4.25	1.06	0.27	0.81	5.64	8.03	100.00
Mean		31.88	32.73	0.47	0.56	5.44	8.85	4.25	1.06	0.27	0.81	5.64	8.03	100.00
Std. deviation		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Max.		31.88	32.73	0.47	0.56	5.44	8.85	4.25	1.06	0.27	0.81	5.64	8.03	
Min.		31.88	32.73	0.47	0.56	5.44	8.85	4.25	1.06	0.27	0.81	5.64	8.03	

All results in weight%

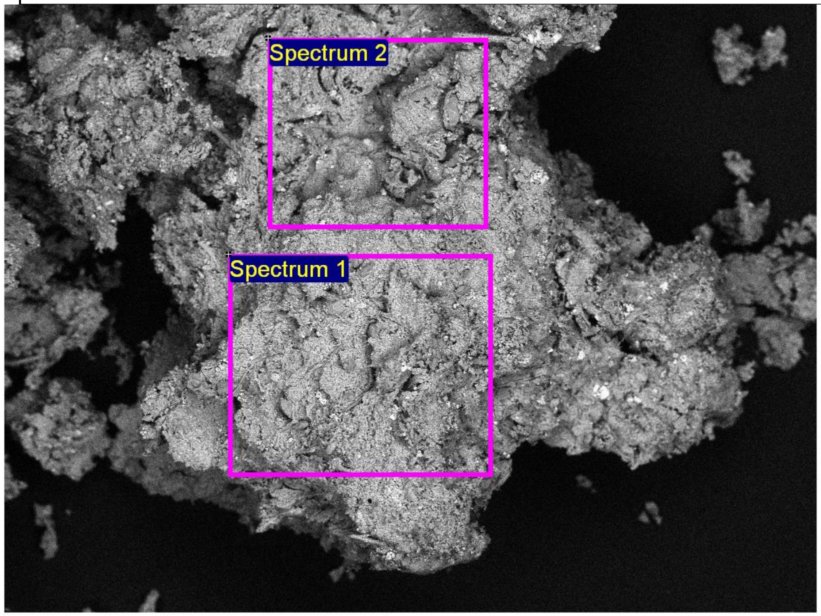
Project 1

2/23/2023 9:45:16 AM

Project: Project 1
Owner: INCA
Site: Site of Interest 1

Sample:
Sacrificial sludge – cut surface

Comment:



Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	O	Na	Mg	Al	Si	P	S	K	Ca	Fe	Total
Spectrum 1	Yes	8.95	47.36	0.71	0.97	11.29	8.17	6.01	0.53	0.82	5.54	9.66	100.00
Spectrum 2	Yes	4.46	48.30	0.78	1.09	10.84	9.40	6.85	0.53	1.14	5.83	10.78	100.00
Mean		6.70	47.83	0.74	1.03	11.06	8.78	6.43	0.53	0.98	5.68	10.22	100.00
Std. deviation		3.17	0.66	0.05	0.08	0.32	0.87	0.59	0.00	0.23	0.21	0.79	
Max.		8.95	48.30	0.78	1.09	11.29	9.40	6.85	0.53	1.14	5.83	10.78	
Min.		4.46	47.36	0.71	0.97	10.84	8.17	6.01	0.53	0.82	5.54	9.66	

All results in weight%

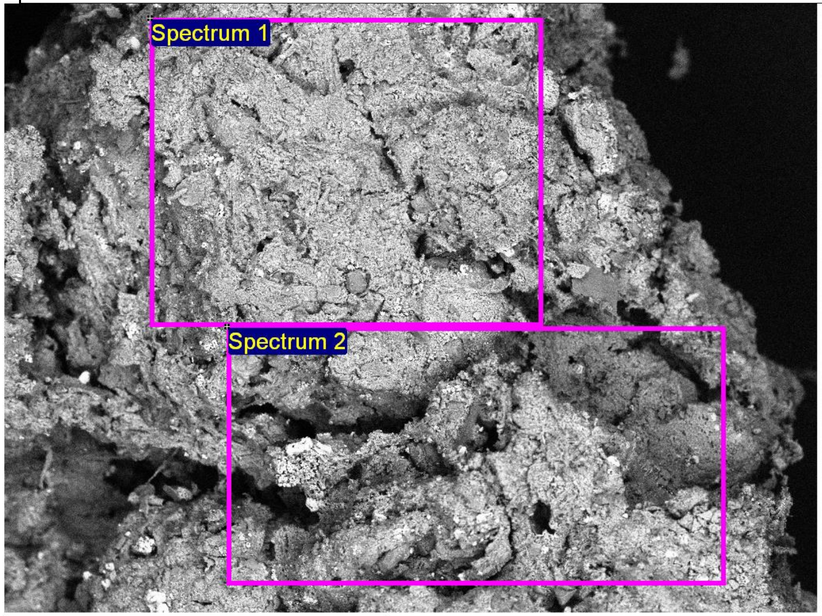
Project 1

2/23/2023 9:45:20 AM

Project: Project 1
Owner: INCA
Site: Site of Interest 2

Sample:
Sacrificial sludge – cut surface

Comment:



Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	O	Na	Mg	Al	Si	P	S	K	Ca	Ti	Fe	Total
Spectrum 1	Yes	10.03	47.62	0.39	0.92	9.14	6.91	9.25	0.27	0.69	5.26	0.51	9.02	100.00
Spectrum 2	Yes	10.73	45.13	0.49	0.99	7.12	7.54	7.91	0.57	0.86	6.35	0.26	12.05	100.00
Mean		10.38	46.37	0.44	0.96	8.13	7.22	8.58	0.42	0.77	5.81	0.39	10.53	100.00
Std. deviation		0.50	1.77	0.07	0.05	1.43	0.45	0.95	0.22	0.12	0.77	0.18	2.14	
Max.		10.73	47.62	0.49	0.99	9.14	7.54	9.25	0.57	0.86	6.35	0.51	12.05	
Min.		10.03	45.13	0.39	0.92	7.12	6.91	7.91	0.27	0.69	5.26	0.26	9.02	

All results in weight%

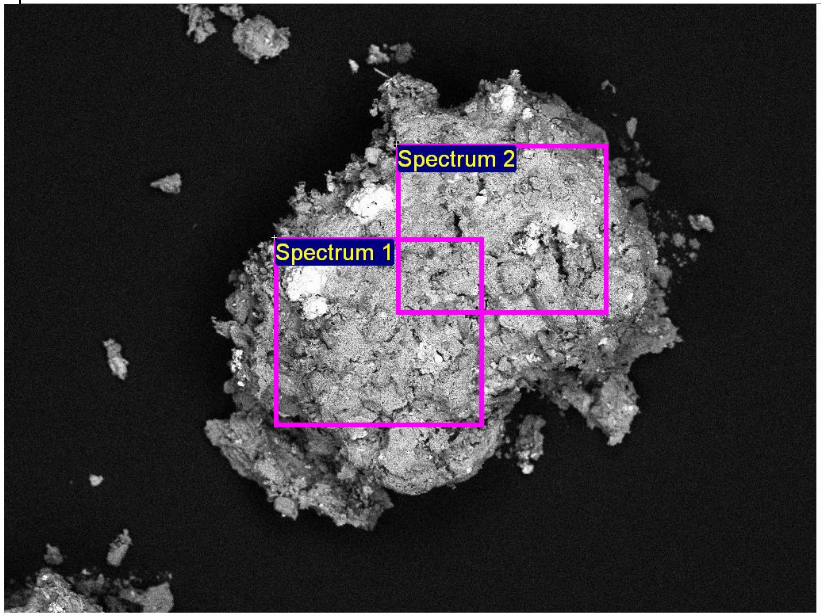
Project 1

2/23/2023 9:45:26 AM

Project: Project 1
Owner: INCA
Site: Site of Interest 3

Sample:
Sacrificial sludge – cut surface

Comment:



Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	O	Na	Mg	Al	Si	P	S	K	Ca	Fe	Total
Spectrum 1	Yes	11.61	44.16	0.46	0.61	6.71	7.02	8.51	0.23	0.91	4.64	15.14	100.00
Spectrum 2	Yes	10.35	44.07	0.62	0.73	7.20	7.09	8.76	0.31	0.92	4.79	15.17	100.00
Mean		10.98	44.11	0.54	0.67	6.95	7.05	8.63	0.27	0.91	4.72	15.16	100.00
Std. deviation		0.89	0.06	0.12	0.09	0.35	0.05	0.18	0.06	0.01	0.10	0.02	
Max.		11.61	44.16	0.62	0.73	7.20	7.09	8.76	0.31	0.92	4.79	15.17	
Min.		10.35	44.07	0.46	0.61	6.71	7.02	8.51	0.23	0.91	4.64	15.14	

All results in weight%

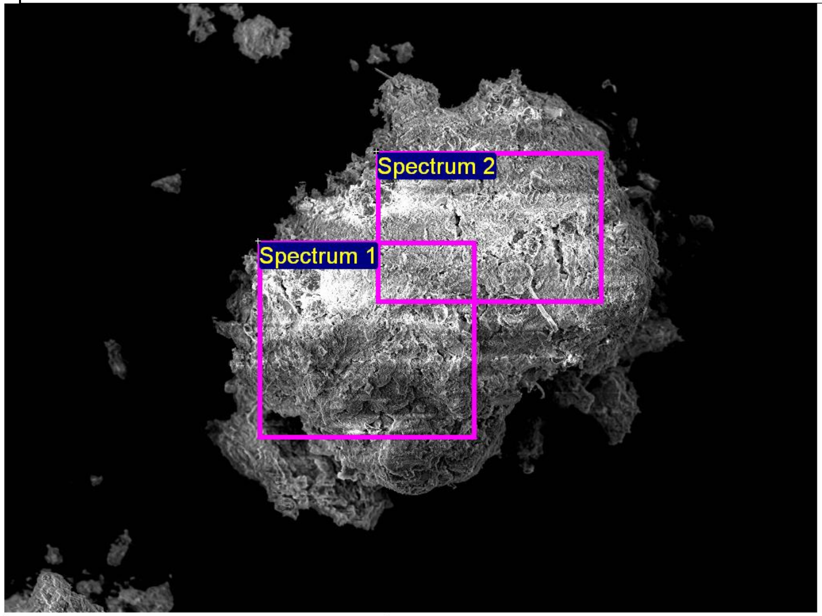
Project 1

2/23/2023 9:45:32 AM

Project: Project 1
Owner: INCA
Site: Site of Interest 4

Sample:
Sacrificial sludge – cut surface

Comment:



Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	O	Na	Mg	Al	Si	P	S	K	Ca	Fe	Total
Spectrum 1	Yes	4.46	47.31	0.67	0.57	8.26	7.73	9.59	0.26	0.96	5.51	14.69	100.00
Spectrum 2	Yes	5.42	46.54	0.65	0.83	7.57	6.94	10.03	0.37	1.14	4.97	15.53	100.00
Mean		4.94	46.93	0.66	0.70	7.91	7.33	9.81	0.32	1.05	5.24	15.11	100.00
Std. deviation		0.68	0.55	0.02	0.19	0.49	0.56	0.31	0.08	0.13	0.38	0.60	
Max.		5.42	47.31	0.67	0.83	8.26	7.73	10.03	0.37	1.14	5.51	15.53	
Min.		4.46	46.54	0.65	0.57	7.57	6.94	9.59	0.26	0.96	4.97	14.69	

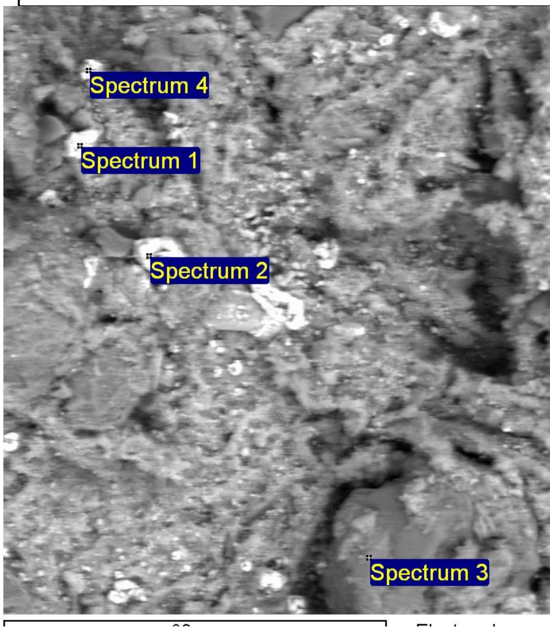
All results in weight%

Project 1

Project: Project 1
Owner: INCA
Site: Site of Interest 5

Sample:
Sacrificial sludge – cut surface

Comment:



Processing option : All elements analysed (Normalised)

Spectrum	In stats.	C	O	Na	Mg	Al	Si	P	S	K	Ca	Fe	Total
Spectrum 1	Yes	3.92	44.36			4.25	30.34	2.57		0.32	1.82	12.43	100.00
Spectrum 2	Yes	4.88	23.16	0.41	0.37	5.49	4.09	2.78			1.89	56.94	100.00
Spectrum 3	Yes		56.92	0.27	0.18	2.05	36.52	1.17	0.25	0.26	0.73	1.66	100.00
Spectrum 4	Yes	5.37	19.64	0.47	0.43	4.44	3.83	5.49		0.53	12.59	47.23	100.00
Max.		5.37	56.92	0.47	0.43	5.49	36.52	5.49	0.25	0.53	12.59	56.94	
Min.		3.92	19.64	0.27	0.18	2.05	3.83	1.17	0.25	0.26	0.73	1.66	

All results in weight%