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Adsorption of PFAS from subsurface using montmorillonite grafted chitosan beads

몬모릴로나이트 접목 키토산 비드를 이용한 표면하에서의 PFAS 흡착

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이 논문을 공학석사 학위논문으로 제출함

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Adsorption of PFAS from subsurface using montmorillonite grafted chitosan beads

Abstract

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Per- and polyfluoroalkyl substances (PFAS) are highly persistent pollutants with widespread contamination in the environment, posing significant risks to human health. To address the urgent need for effective remediation strategies, adsorption techniques have gained prominence as a promising approach for PFAS removal. However, the currently available commercial adsorbents have limitations, such as the lack of studies on their performance in soil, and the use of non-renewable materials. To address these issues, a novel adsorbent based on montmorillonite grafted chitosan beads (MTGCB) is developed that combines the advantages of both natural materials and efficient against PFAS removal. This thesis focuses on the comprehensive analysis of MTGCB for the efficient removal of PFAS from water, stabilization in PFAS-contaminated soil, and their impact on the mechanical properties of the soil and compare them with commercial adsorbent granular activated carbon (GAC).

The introduction highlights the detrimental effects of PFAS on human health, emphasizing the critical need for effective remediation strategies. Adsorption techniques, such as those employed in this study, are instrumental in removing PFAS from water, stabilizing contaminated soil, and enhancing the mechanical properties of the soil. The research comprises three main components: (1) adsorption tests to evaluate the efficiency of MTGCB and GAC for PFAS removal from water, (2) leaching tests to assess the stabilization properties of these adsorbents in soil, and (3) shear parameter analysis to investigate the impact of the adsorbents on the mechanical properties of the soil.

The results demonstrate that both GAC and MTGCB exhibit effective removal of PFAS compounds, with higher removal rates observed for long-chain PFAS compounds. GAC shows excellent adsorption capacity, reaching equilibrium within 24h for all PFAS compounds, while MTGCB exhibits 48h except PFBA which is 24h due to its molecular size. Both adsorbents conform well to the Langmuir and Freundlich model, and MTGCB demonstrates higher capacity for PFOS, PFBS and PFBA due to hydrophobicity and electrostatic interactions, while for PFOA it was similar to GAC. Leaching tests indicate that GAC provides excellent stabilization with minimal leaching, while MTGCB shows a decreasing trend in leaching with increasing adsorbent percentage. Longer carbon chains and sulfonic groups in PFAS contribute to better stabilization. Optimal addition percentages of 2% for GAC and 10% for MTGCB are recommended for achieving soil stabilization. Furthermore, compaction tests reveal a decrease in maximum dry unit weight of soil with the addition of both adsorbents due to their low specific gravity and increased water content in GAC due to presence of its water holding capacity while in MTGCB the variation was negligible. However, the friction angle and cohesion increase, indicating improved mechanical properties, with GAC's

angular shape and MTGCB's presence of montmorillonite aiding in binding soil particles together. An optimal addition percentage of 5% is suggested for achieving enhanced mechanical properties. Considering the stabilization and mechanical properties of the soil, the optimal addition percentage of MTGCB is found to be 10%, while for GAC, 2% addition is determined to be effective.

Overall, this research highlights the potential of MTGCB as a promising alternative to GAC for the stabilization of PFAS in soil. MTGCB demonstrates comparable adsorption performance, effective leaching control, and the ability to improve soil mechanical properties. The findings provide valuable insights for the application of these adsorbents in PFAS removal and soil stabilization, contributing to the development of efficient soil remediation strategies and environmental risk assessments.

Keywords: PFAS, remediation, adsorption, natural adsorbent, chitosan, montmorillonite, activated carbon, leaching, stabilization, shear parameter.

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Chapter 1: Introduction

1.1 Study background

Chemicals containing a C-F backbone and a functional head group, such as a carboxylate, sulfonate, or amide, are referred to as per- and polyfluoroalkyl substances (PFASs) (Gallen et al. 2017). Per- and polyfluoroalkyl substances (PFAS) are synthetic chemicals that are often used in industrial and commercial sectors. They are used as foaming, lubricating, and surfactant agents as well as basic elements for fluoropolymers (Lau et al. 2012, Schultz et al. 2003). Due to the PFASs' extensive use and resistance to degradation, they have accumulated in soil, groundwater, and aquifers all over the world and contaminated them (Gellrich et al. 2012, Murakami et al. 2009). Since PFAS are so persistent in the environment, research have shown that they cause bioaccumulation in living things (Haukås et al. 2007, Lesmeister et al.2021). PFAS were found in almost all serum samples from the general population, according to the National Health and Nutrition Examination Survey (NHANES), indicating widespread exposure in the US (CDC, 2009). PFAS exposure has been linked to a number of cancers, immune system problems, reproductive problems, and liver toxicity (DeWitt et al., 2019; Saikat et al., 2013; Shearer et al., 2020).

The highest PFAS contamination was detected in surface water relative to ground, tap, and drinking water. PFAS levels in water resources in several countries in Asia, such as China, Japan, and South Korea, were above the recommended level, similar to that in the United States (Jobriell et al. 2021). In South Korea various types of PFASs such as PFOA, PFOS, PFPeA, PFHxA, PFBA, PFPeS, PFBS, PFHxS were seen above the EPA water health advisories (Kim et al. 2021). Among these most common PFASs were PFOA,

PFOS, PFBA and PFBS in water (Lee et al. 2020). The locations of these contaminated water were Nakdong river, Asan lake and effluents of waste water treatment plants of Daegu and Gumi (Kim et al. 2021, Lee et al. 2020, Choi et al. 2021). A nationwide monitoring of perfluoroalkyl substances (PFAS) in soils was conducted for various land-use types around South Korea, such as industrial complexes, landfills, farmlands, mountains, and woodlands. It was reported the presence of various PFAS, among them PFOS, PFOA and PFCAs were predominant (Sam et al. 2021). In Cheongju-si & Chungcheongbuk-do it was reported on human serum that PFOA and PFOS is above the limit of German Human Biomonitoring Commission (Heo et al. 2022).

Destructive and nondestructive methods are commonly used in PFAS treatment technologies (N. Merino et al. 2016, N.B. Saleh et al. 2019). Destructive methods are designed to damage the PFAS molecules' strong C-F bonds and break them down into more harmless molecules (preferably fluoride, carbon dioxide, and water) (N. Merino et al. 2016). For the treatment of PFAS, including PFOA and PFOS, a variety of destructive procedures, including chemical oxidation, advanced reduction, electrochemical oxidation, photocatalysis, sonochemical therapy, hydrothermal reaction, plasma treatment, and thermal destruction, have been researched (J. Cui et al. 2020, Radjenovic et al. 2022, Singh et al. 2019). These approaches have shown some early promise in the elimination and defluorination of PFOA and/or PFOS, primarily in laboratory studies. Adoption of these early-stage technologies calls for more thorough research on a number of issues, including the identification of intermediate and end products, the analysis of degradation pathways, field demonstration, etc. (N.B. Saleh et al. 2019, J. Cui et al. 2020, Ross et al. 2018, Wanninayake et al. 2021). In contrast, nondestructive technologies including adsorption, reverse osmosis, and nanofiltration work

to physically separate and concentrate PFAS quickly (Du et al. 2014, J. Wang et al. 2018, N.J. Herkert et al. 2020).

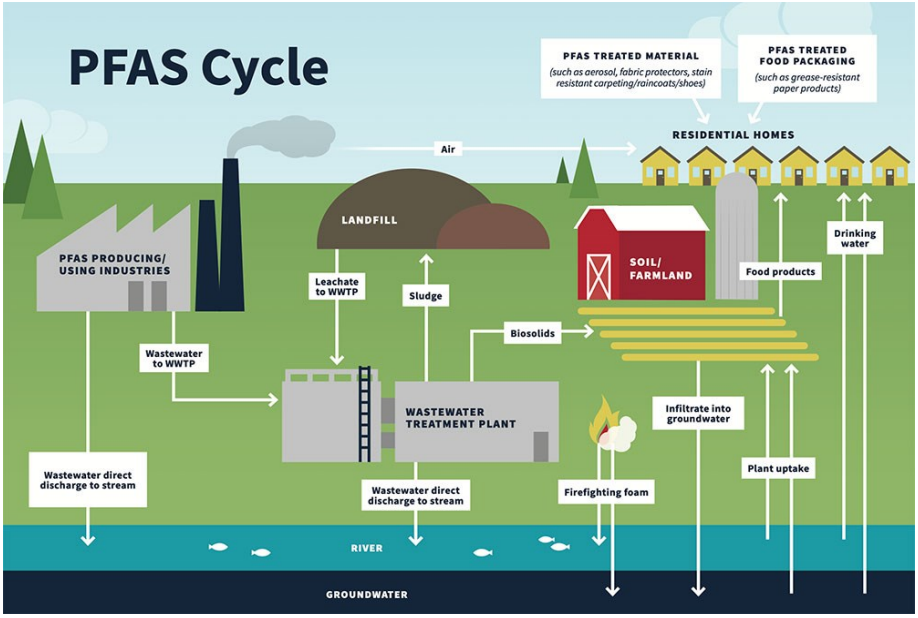

Figure 1.1 PFAS movement in the environment (Michigan Dept. Environmental Quality)

Ion exchange and granular and powdered activated carbon (GAC/PAC) sorption are now the most popular methods for removing PFAS, and both have been used successfully in various field applications. (Z. Du et al. 2014, V.A.A. España et al. 2015). However, Traditional GAC/PAC and ion exchange resins have a number of drawbacks, including slow sorption kinetics, a lack of selectivity, and poor performance in the presence of organic matter and other water constituents (E. Gagliano et al. 2020, D. Zhang et al. 2019). Activated carbon or non-ionic resins with low charge density do not display appropriate affinity since the predominant PFASs present in contaminated waters are anionic and highly hydrophilic, which results in low treatment efficiency and high treatment costs (Ross et al., 2018). Microbial denitrification and nutrient

availability have been demonstrated to be decreased by AC (Bonaglia et al., 2020). Due to the widespread natural abundance of clay minerals, small physical space between clay particles, easy separation from the contaminant, negligible harmful effects on the ecosystem and modified clay shown higher removal capacity of PFAS (Mukhopadhyay et al. 2021). Chitosan is a well-known material derived from natural organic biomass and has obtained global attention for its unique physicochemical properties (Aranaz et al. 2021). Poly(ethylenimine) (PEI)-functionalized cellulose microcrystals (PEI-f-CMC) have been explored for removing 22 PFAS, including legacy and emerging carboxylic and sulfonated PFAS and PFAS-precursors, from aqueous solutions at environmentally relevant concentrations (M. Ateia et al.2018).

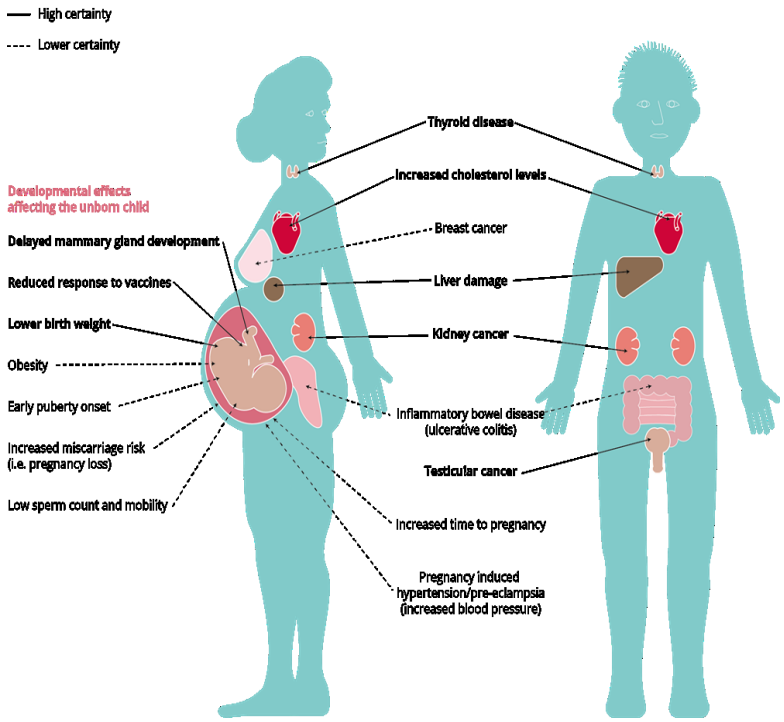

Figure 1.2 Health effects due to PFAS exposure (European Environmental Agency

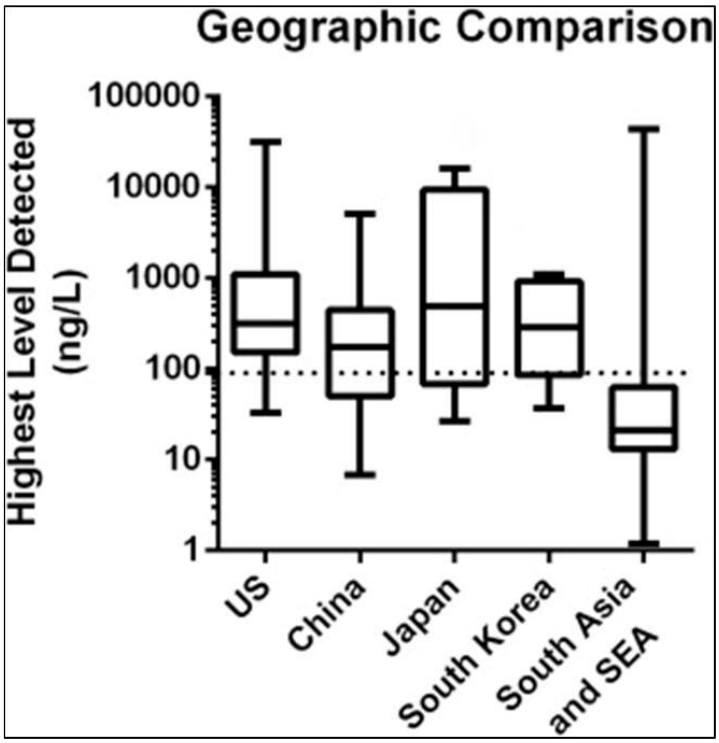

Figure 1.3 Comparison of PFAS levels in US and Asian water resources, with recommended threshold indicated by Swedish national food agency (Jobriell C.Baluyot et al., 2021).

1.2 Purpose of research

The primary focus of this thesis is to explore the potential of utilizing cost-effective and environmentally friendly materials, namely montmorillonite and recycled chitosan, as adsorbents for removing per- and polyfluoroalkyl substances (PFAS) from water and leaching in contaminated soil. The study aims to evaluate the effectiveness of these materials compared to commercially available adsorbents like granular activated carbon (GAC). Additionally, the study aims to assess the reusability of the montmorillonite grafted chitosan bead (MTGCB) adsorbent and its impact on the geotechnical properties of soil when mixed together. The findings from this research will provide valuable insights into the application of sustainable and cost-effective materials for PFAS removal and their potential integration into environmental remediation practices.

The combination of montmorillonite and chitosan forms a unique structure with excellent chemical stability and a high affinity for PFAS. The addition of grafted polyethyleneimine enhances the adsorption capacity of the beads, enabling effective removal of PFAS from contaminated media. Furthermore, the utilization of low-cost and environmentally friendly materials such as montmorillonite and chitosan offer a sustainable and economically viable alternative to conventional adsorbents, making it a promising solution for PFAS remediation in soil and water.

Therefore, the study aims to assess the performance of the Montmorillonite grafted polyethyleneimine chitosan bead (MTGCB) adsorbent through batch adsorption tests, specifically focusing on the removal of PFAS from the aqueous phase. Additionally, the leaching potential of MTGCB in contaminated soil will be investigated through batch leaching tests

using deionized water. The examination of leaching effects mixed with adsorbent in soil is an understudied aspect in the field of PFAS remediation, making this research particularly significant in advancing the understanding of MTGCB's efficacy as an adsorbent.

Moreover, the research recognizes the importance of evaluating the geotechnical characteristics of MTGCB as an adsorbent for remediating PFAS. Consequently, the study also aims to assess the influence of MTGCB on the geotechnical properties of soil through compaction and direct shear tests. These assessments will provide valuable insights into the practicality of employing MTGCB as an efficient and environmentally friendly solution for PFAS remediation in soil and water environments.

Chapter 2: Literature review

2.1 Adsorption

Adsorption treatment has become an increasingly popular method of removing contaminants from soil and water, as it is generally cost-effective and can be a more efficient process than other methods. Adsorption treatment for contaminants in soil and water has several advantages. According to RK Ibrahim et al. (2016), it is a useful technology for removing organic and inorganic pollutants from contaminated water sources. The authors point out that it is a relatively inexpensive, low-maintenance approach that can be used to treat large volumes of water or soil. Furthermore, adsorption treatment can be used to remove a wide range of pollutants, including heavy metals, organic compounds, and suspended solids. Moreover, it is an effective technology for achieving a high removal efficiency. As has been demonstrated in various studies, adsorption treatment can be used to reduce contamination levels to below the allowable limits. Finally, the authors note that adsorption treatment can be easily integrated into existing water treatment systems, making it a viable option for many industrial and municipal applications.

Adsorption treatment of contaminants in soil is a promising method to address the problem of soil contamination. KY Foo and BH Hameed (2009) suggest that this method is widely used due to its cost-effectiveness and simplicity. Adsorption treatment involves the use of substances known as adsorbents, which can reduce the concentration of contaminants in the soil by binding them to their surface. It is often used in combination with other methods, such as physical and chemical treatments, to increase the overall efficiency of the process. Adsorption has been found to be effective in removing heavy metals, pesticides, and other organic pollutants from soil.

However, there are still some limitations to this method, such as its inability to completely remove contaminants or its short-term effectiveness. Despite these drawbacks, adsorption treatment is an important tool for the remediation of contaminated soils and should be further studied to expand its potential applications.

In addition, the adsorption process produces fewer byproducts than other water treatment processes, which helps to minimize the environmental impact of the treatment and also beneficial in terms of reducing the potential for leaching of contaminants into water bodies (Dai et al. 2019). Overall, adsorption treatment can be beneficial for both the environment and human health, making it an efficient and cost-effective treatment option. Adsorption treatment is a relatively novel method for cleaning up contaminated soil and water sources, and it has the potential to be a cost-effective alternative to more traditional methods. This treatment relies on adsorbent materials, to capture pollutants, without necessarily requiring the use of large-scale machinery or extra manpower. However, this solution is not a catch-all, and must be tailored to the specific conditions and needs of each site, as different types of pollutants may not be amenable to adsorption. Additionally, due to the often hard-to-predict dynamics of soiling and runoff, long-term efficacy of this type of treatment should be monitored, to ensure it is behaving as intended.

In soil and water, adsorbent is applied by mixing with them. Adsorption is a recognized method for removing PFAS, both as a standalone procedure for point-of-use applications and as a phase in water treatment facilities (Arvaniti et al. 2015, Eschauzier et al. 2012). The most common adsorbents used for treatment in water is activated carbon, ion exchange resins or polymer (Dushanthi et al. 2021). To lower the concentration in the leachate in soil, the adsorbent in this situation will absorb the contaminants and immobilize them.

Studies that combined PFAS-contaminated soils with adsorbents including GAC, Biochar, and modified clays have demonstrated that this is an effective technique (Das et al. 2013, Barth et al. 2021). To date, the immobilization by adsorption method has been a significant part of the remediation solution for PFAS contaminated soils, although its long-term efficiency still needs further investigation ((Mahinroosta & Senevirathna, 2020). Previous research on the adsorption of organic pollutants on various adsorbents have reported a number of interactions, including the hydrophobic effect, electrostatic interaction, ion exchange, Van der Waals forces, hydrogen bond, and π–π bond (Teymourian et al. 2021). The bond of π–π, however, is improbable to form in the adsorption of the per fluorinated compound due to the lack of π electrons in their structure, and the Van der Waals force is also insignificant due to the small molecular sizes and low polarizabilities of the per fluorinated compounds (Z. Du et al. 2014, S. Deng et al. 2012). The primary mechanisms that regulate PFAS adsorption include the hydrophobic effect, electrostatic interactions, and formation of micelles or hemimicelles (self-aggregation) (I.M. Militao et al. 2021).

2.2 Leaching test

Leaching tests are made to determine how much of a constituent is released and to evaluate the factors that could influence that release. To evaluate the potential leaching and mobility of pollutants from soils or wastes, typically under scenarios of disposal in landfills, many standard operating protocols have been devised (Scott, J et al. 2005). In order to classify wastes for proper disposal, leaching studies, which are based on batch equilibration of soil with desorption solutions (Scott, J et al. 2005).

Batch equilibrium leaching tests typically depict constituent leaching while considering a number of variables, including adjusting the extractant pH, the liquid-to-solid ratio, and leaching time. The U.S. Environmental Protection Agency Toxicity Characteristic Leaching Procedure (TCLP) (U.S.EPA, 1992) is a commonly employed extraction test with regulatory significance. It is specifically designed to simulate a worst-case scenario for the mobilization of contaminants in landfills that contain municipal solid waste (Scott et al., 2005). The TCLP utilizes an acetic acid solution with a pH of either 2.9 or 4.9, depending on the alkalinity of the waste. By subjecting the waste to these acidic conditions, the test aims to assess the potential for leaching of hazardous constituents into the environment.

In the context of assessing contaminant mobilization from soils, the Synthetic Precipitation Leaching Procedure (SPLP) was developed. The SPLP replicates the conditions of acidic rain, simulating the leaching process under such scenarios. It employs a solution with a pH of either 4.2 or 5.0, which corresponds to the acidity of the precipitation (U.S.EPA, 1994). This test provides insights into the release potential of contaminants from soils, particularly in situations where acidic rain events may occur.

These extraction tests, such as the TCLP and SPLP, have gained widespread adoption and have been utilized by various jurisdictions. For instance, the Australian Standard Leaching Procedure (ASLP, 4439.3–1997) has been developed as a variant of these methods. The ASLP specifies the leaching of waste using different leaching fluids, including water, acetic acid at pH 5.0, or a buffered solution with a pH of 9.2. The selection of the appropriate leaching fluid depends on the specific type of landfill being assessed (Scott et al., 2005). By incorporating variations of these tests, regulatory frameworks can assess the leaching potential of contaminants from

different waste materials and soils, aiding in effective environmental management and mitigation strategies. ASLP leaching test were done in different studies under the water conditions to give more environment related conditions (Kabiri, S. et al. 2021, Rayner et al., 2022, Juhasz et al. 2022)

Only a few studies have employed these common tests to evaluate the potential leaching of PFASs from soils, despite the fact that they have been used to evaluate a wide range of inorganic and organic pollutants in soils, sediments, and wastes. There aren't many papers that discuss the leaching tests used to look into PFAS stability in contaminated soils following sorbent remediation. Sörengrd et al. 2019 assessed the leachability of several PFASs following remediation with colloidal activated carbon using a dynamic leaching test that followed a comparable technique to the European standard compliance leaching test EN12457-128. Leaching of various PFASs from soil was assessed in another investigation utilizing a leaching test in water following stabilization with various sorbents (Bräunig, J. et al. 2021) and solidification with cement (Sörengård et al. 2019). To assess the effectiveness of in situ remediation of AFFF-contaminated soils using two commonly used sorbent materials, a number of leaching tests, including ASLP, MEP, and LEAF (1313 and 1314) were performed (Kabiri, S. et al. 2021 and Kabiri, S. et al. 2021).

2.2.1 Environment regulations for PFAS

The presence of Per- and Polyfluoroalkyl Substances (PFAS) in soil and water has become an increasing source of concern for environmental regulators. TG Ambaye et al. (2022) investigate the sources of PFAS contamination in soil and water in their study Science and Pollution. They found that the primary sources of PFAS contamination in soil and water are industrial discharges and wastewater effluents. A study conducted by E Panieri,

K Baralic, D Djukic-Cosic, A Buha Djordjevic, et al. (2022) examined the impact of PFAS on the environment and human health. The study found that PFAS have been linked to a variety of environmental and health issues, including ecological damage, contamination of drinking water sources, disruption of endocrine systems, and negative impacts on fertility, reproductive health, and cancer risk. The study concluded that it is essential to reduce and regulate the use of PFAS in order to protect the environment and human health. This is especially true given the potential for long-term and cumulative damage caused by PFAS. (Panieri et al., 2022).

Regulatory measures have been proposed to reduce the presence of PFAS in soil and water. According to GL Carlson and S Tupper (2020), regulatory and non-regulatory measures can be used to reduce PFAS pollution in the environment. Regulatory measures involve the adoption of laws and standards to control the use of PFAS, as well as the development of risk management plans to identify sites with high PFAS levels and reduce the risk of PFAS contamination. Non-regulatory measures include the use of education and outreach programs to raise awareness about the risks associated with PFAS exposure and to encourage individuals to take steps to reduce their PFAS exposure. In addition, best management practices (BMPs) can be used to reduce PFAS pollution, such as the implementation of green infrastructure to capture runoff and prevent it from entering surface water and groundwater. Finally, reducing or eliminating the use of PFAS-containing products, such as firefighting foam, paints, and non-stick coatings, can help to reduce the levels of PFAS in the environment. Overall, the implementation of both regulatory and non-regulatory measures is essential for reducing PFAS pollution in soil and water. (Carlson & Tupper, et al. 2020).

Only a small number of nations have environmental standards on PFAS in soil. PFAS regulations in both soil and water for Asian countries did not appear in any internet searches. Japan and South Korea, for example, abide with US EPA environmental rules. There isn't a specific PFAS regulation for soils in US, state guidance and policy of US EPA show for certain states such as Delaware, West Virginia, and Wisconsin, have soil screening standards of 6,000 and 16,000ng/g (PFOS and PFOA), 240,000ng/g (PFOA), and 1,260ng/g (PFOS and PFOA in non-industrial areas), respectively. Table 2.1 & 2.2 displays the environmental laws governing PFAS in several nations.

Table 2.1 Permissible limits of PFAS in soil for different countries

Country	**Soil limit(ng/g)**	**References**
Denmark	390 (PFOS & PFOSA), 1300 (PFOA)	Danish Ministry of the Environmental Protection Agency (2015)
Netherland	1.4 (PFOS) & 1.9 (PFOA)	RIVM 2020
Canada	10,140 & 210 (PFOS-Agricultural, Residential and Commercial)	Environment and Climate Change Canada (2017)
Germany	100 (sum of PFOA & PFOS)	Guidelines for PFAS assessment of Germany, 2022
Australia	1000 (PFOS) & 10,000 (PFOA)	PFAS (NEMP Version 2.0, 2020)

Table 2.2 Permissible limits of PFAS in water for different countries

Country	Water limit(ng/l)	References
Denmark	100 (PFOA,PFOS,PFNA,PFBA/S,PFHxS/A.PFPeA, PFHpA, PFOSA,PFDA,6:2 FTS)	EPA 2015 Chohan et al. (2021)
Netherland	530 (PFOS)	RIVM 2011
Sweden	90 (PFOA,PFOS,PFBS,PFHxS,PFHxA,PFPeA,PFHpA)	NFA 2014 Chohan et al. (2021)
Germany	100 (PFOA & PFOS)	GMOH 2006 (M. K. Kim et al., 2012)
Australia	560 (PFOA) & 70 (Sum of PFOS & PFHxS)	PFAS (NEMP Version 2.0, 2020)
U.S.	70 (PFOA & PFOS)	USEPA 2016 Cordner et al. (2019)
Canada	200 (PFOA) & 600 (PFOS)	CELA 2019
South Korea	480 (PFHxS) & 70 (sum of PFOA & PFOS	Ministry of Environment of ROK 2019

2.3 Low cost materials

In recent years, there has been a push to create more sustainable and cost-effective methods to reduce the presence of PFAS in water and soil. The use of low cost or recyclable materials for adsorption of PFAS is becoming increasingly popular due to its potential environmental and economic benefits. Conventionally, carbonaceous materials like activated charcoal and anion exchange resins are frequently used (Ateia et al. 2019). Polymer-based synthesized adsorbent materials also increase PFAS removal due to the adsorbent's affinity and porosity. However, their adsorption capacity is reported in the ranges of 10 to 100 mg PFAS per g (Shih and Wu 2020). Recently, amine-based adsorbent synthesized material (e.g., chitosan, polyaniline) was more effective in PFAS removal and displayed a greater affinity for PFAS adsorption than carbonaceous material and non-ionic material resin (Vo et al. 2020).

In a recent study by Melo et al., 2022, among others, the potential of natural polymers for adsorption of perfluoroalkyl substances (PFAS) from soil was evaluated. The authors examined the characteristics of different natural polymers and their advantages for PFAS adsorption. They found that natural polymers have several advantages over artificial polymers, including biodegradability, low toxicity, high specific surface area, and low cost. For example, natural polymers have a greater capacity for adsorption compared to synthetic polymers, indicating that they may be better suited for PFAS remediation. Additionally, natural polymers are renewable, so they offer a sustainable solution to PFAS contamination in soils. The use of in situ PFAS adsorbent based on naturally abundant geogenic materials is a promising option due to low costs and toxicity. Clay minerals are mostly hydrophilic and negatively charged, therefore they can poorly adsorb the anionic and

hydrophobic PFAS compounds. Agents such as polymers, surfactants, amines, micro- and nano carbon particles are being used to modify clay minerals and improve its adsorption capacities (Mukhopadhyay et al., 2021). The hydrophobicity of clay minerals is enhanced due to its modification with polymers, leading to an efficiently removal of negatively charged hydrophobic contaminants such as PFAS (Mukhopadhyay et al., 2021)

The recent study conducted by R Mukhopadhyay, B Sarkar, KN Palansooriya et al. (2021) on clay-based natural adsorbents for PFAS removal was highly insightful. Clay-based natural adsorbents are an emerging class of materials that can be used for the efficient removal of PFAS from water. Plant-based natural adsorbents have been studied extensively as a potential solution to PFAS removal from water. In a study conducted by R Zocchi et al. (2022), the efficacy of natural adsorbents for PFAS removal from water was explored. The authors focused on transition metal oxides, activated carbon, and plant-based natural adsorbents. The results of the study indicated that plant-based natural adsorbents demonstrated the most promising PFAS removal ability. Plant-based adsorbents have unique structure and surface chemistries that allow them to bind PFAS to their surfaces via a variety of mechanisms, including hydrogen bonding, electrostatic attraction, and hydrophobic interaction. The authors observed that the most effective plant-based adsorbents for PFAS removal from water were lignocellulose, chitosan, and alginate. These adsorbents are abundant, biodegradable, and generally non-toxic, making them attractive solutions for PFAS removal. The authors also noted that the effectiveness of plant-based adsorbents can be improved by modifying their surface chemistry and structure.

There is a wide variety of natural adsorbents that can be used to remove PFAS from water and other liquids. These natural adsorbents can often times

be more effective than synthetic materials for removing PFAS, and have the added benefit of being less expensive and more environmentally friendly. With the growing demand for PFAS removal from water and soil, natural adsorbents are becoming increasingly popular and have great potential for the future.

2.3.1 Montmorillonite

Montmorillonite is a clay mineral that is part of the smectite group and is known for its high swelling capacity in water and cation-absorption ability. Its large surface area allows it to strongly bond with cations, making it useful for various applications, including adsorption of toxic pollutants, soil amendment, insulation, drilling muds, and as a component of paints and coatings (Occelli and Tindwa 1983). Montmorillonite has a unique structure that consists of two layers of silicate sheets, a central layer of octahedrally coordinated metal ions, and a tetrahedral sheet held together by hydrogen bonds ((Zoveidavianpoor, 2018). Its interlayer cations can be exchanged with other cations, making it suitable for adsorption, cation exchange, and catalytic reactions (Zoveidavianpoor, 2018). Montmorillonite has a relatively high cation exchange capacity, which makes it useful for many industrial applications such as wastewater treatment, cement additive, fertilizer, soil conditioner, and cosmetics (Chen and Curliss 2003). It is composed of hydrated aluminum silicate, potassium, calcium, and magnesium, and has the ability to remove various pollutants such as heavy metals, organic pollutants, and dyes from water (Chen and Curliss 200), Z. Li et al. 2016, Zhao et al. 2020). Synthetic montmorillonite (SMM) has also been shown to effectively remove various organic contaminants and heavy metals from wastewater (Lin and Juang 2009)

South Korea has been a major contributor to the global market for montmorillonite clay since the 1990s, with the industry expanding rapidly due to government support. The clay has been used in Korea since the Neolithic period for pottery, medical treatments, and food production, such as kimchi. South Korea produces several varieties of montmorillonite with high surface area and cation exchange capacity, making it a desirable additive for food, pharmaceutical, and health care products. Additionally, the country is a significant supplier of montmorillonite for the paper industry, as it can increase the strength and durability of paper products. The Korean montmorillonite clay industry generates over US$500 million annually and has become a major global player in the production of montmorillonite and its derivatives. (Harvey & Murray, 1997; Islam et al., 2015; Murray et al., 2002; Karim et al., 2009).

Montmorillonite clay adsorbents have been found to have the potential to adsorb poly- and perfluoroalkyl substances (PFAS) from contaminated water sources, according to a recent article by R Mukhopadhyay, B Sarkar, KN Palansooriya, et al. published in Advances in Colloid and Interface Science (2021). The authors highlight the many benefits of using montmorillonite clay adsorbents for PFAS adsorption, including their availability, low cost, and biodegradability. Additionally, montmorillonite clay adsorbents have a high surface area, which allows them to adsorb a large amount of PFAS. Furthermore, they are highly pH-resistant, which allows them to be used in a wide range of pH conditions. Moreover, they can be used in both liquid and solid phase adsorption processes, depending on the application. Low-cost natural montmorillonite (hydrated aluminum oxide, Mt) clay was applied in PFAS adsorption. Results show that the layered structure of Mt clay provides abundant adsorption sites for PFAS through hydrophobic interaction, electrostatic interaction, and hydrogen bonding (Phillips et al. 2021). Du, Z et al. (2016) demonstrated selective and strong adsorption of PFOA and PFOS

using a fluorinated montmorillonite (F-MT) synthesized via the intercalation of fluorinated cationic surfactants (PFQA) into interlayers of the montmorillonite. Montmorillonite-HDTMA, Montmorillonite-HDTMA and 3-indole-acetic acid, Montmorillonite-Poly(m-phenylene isophthalamide)/organic compounds, Montmorillonite-HDTMA and poly-4-vinylpyridine-co-styrene mixture all these adsorbents shown a removal efficiency of PFAS more than 90% (W. Liu et al. 2013, Tian et al. 2016, Luo et al. 2016, Z. Chen et al. 2019). The major mechanisms of these modified montmorillonite clay were electrostatic attraction (Luo et al. 2016) & hydrophobic interaction (W. Liu et al. 2013). Finally, montmorillonite clay adsorbents are non-toxic and environmentally friendly, making them an attractive option for PFAS removal. Nutrient amended clay has shown better result to decrease the chemical bioavailability from soil and translocation to plants while removing PFAS (Hearon et al. (2021))

2.3.2 Chitosan

Chitosan, a copolymer of N-acetyl-d-glucosamine and d-glucosamine, is available in different grades depending on the degree of acetylated moieties. It is a polycationic polymer that has one amino group and two hydroxyl groups in the repeating glucosidic residue. Its carbohydrate backbone is very similar to cellulose, except that the acetylamino group replaces the hydroxyl group on the C2 position. Chitosan is obtained by the thermochemical deacetylation of chitin, a naturally occurring polymer and the second most abundant polysaccharide in nature. The source of chitin is the shell waste of crustacea, insects, and some fungi, and it is harvested annually in several million tons. Chitosan has a rigid crystalline structure through inter- and intra-molecular hydrogen bonding after refinement. The biopolymer represents a cheap and readily available source, and hence it has a wide range of applications in

various fields such as agriculture, food, cosmetics, and biomedical sciences. (F. Hoppe-Seiler et al. 1994, Samanta (2009), Roberts 1992, C.K. Rha et al. 1984, H. Struszcyk et al. 1992)

Chitosan is a natural biopolymer with diverse applications in food, cosmetics, and pharmaceuticals, and South Korea has seen a remarkable growth in chitosan production in recent years. The surge in production and demand can be attributed to technological advances, reduction in costs associated with production, and the increasing demand for chitosan-based products from abroad. According to HK No and SP Meyers (2004), South Korea's chitosan production capacity has increased by nearly three times in the past decade, and Piasecka-Zelga et al. (2021) report that South Korea's market share of chitosan has increased from 4.6% in 2014 to 6.5% in 2020. The South Korean government's policies and initiatives to promote research and development of chitosan-based products, providing subsidies to manufacturers, and encouraging innovative chitosan-based products have contributed significantly to the growth of the industry. Additionally, South Korea's increasing number of patents for chitosan products and research and development initiatives related to chitosan have boosted the competitiveness of South Korean producers in the global marketplace. Consequently, South Korea has become a major player in the global chitosan market, with its high-quality and competitively priced products meeting the rising demand for chitosan globally.

Chitosan are becoming more popular as adsorbents for different contaminants, including heavy metals ((Wang & Chen, 2014)), antibiotics (Afzal et al., 2018), and dyes (Rashid et al. 2017). A study conducted by (He et al. 2022) investigated the characteristics of modified chitosan adsorbent and its efficiency in adsorbing PFAS. The study found that the modified chitosan

adsorbent contains a high amount of amine groups, as well as a high surface area and pore volume, which are essential for effective adsorption of PFAS. The adsorption capacity of the modified chitosan adsorbent was also significantly higher than that of other adsorbents. The study showed that the adsorption efficiency and capacity of the modified chitosan adsorbent for PFAS were strongly dependent on the pH of the solution and the type and concentration of the PFAS. Novel chitosan–ethylene glycol hydrogel for the removal of aqueous perfluorooctanoic acid was found to be effective (Long et al. 2019). Furthermore, the modified chitosan adsorbent was highly stable and reusable, making it a cost-effective and sustainable option for PFAS removal (IM Militao et. al 2021).

2.3.3 Poly(ethylenimine)(PEI)

PEI (Polyethylenimine) production has a long history in South Korea, dating back to 2006 when SH Kim, H Mok, JH Jeong, and SW Kim published their work in Bioconjugate Chemistry on the topic. Since then, the country has made tremendous strides in the production of PEI, with a particular focus on the development of bioconjugates. Through their research, the authors identified the potential for PEI to be used as a versatile platform for the synthesis of bioconjugates. Additionally, they noted the importance of PEI in providing a reliable source of bioconjugates for a variety of applications, such as drug delivery and targeted therapies. This research has been instrumental in paving the way for the development of a thriving industry in South Korea. South Korea is one of the world's leading producers of electronic devices, which rely heavily on the use of gold for their manufacturing and also committed to promoting eco-friendly and sustainable products. The paper (Yun et al. 2020) demonstrate that PEI plays a critical role in the adsorption process due to its amine groups that can form complex bonds with gold ions

and thus helps in efficient recovery of gold. The global PEI market was valued at US$ 408.78 Million in 2021 and is forecast to reach value of US$ 478.78 by 2030 (Coherent Market Insights, 2022). According to MarketWatch 2023, South Korea is one among the 4 major countries which produce PEI in Asia. As a result, South Korea has become a major contributor to the global market and a leader in the production of PEI.

PEI is a cationic polymer with a linear polymer backbone of repeating units of ethyleneimine (C_2H_5N) and branches of primary, secondary, and tertiary amine groups. The properties of PEI are influenced by its molecular weight, degree of branching, and degree of protonation. The high degree of protonation and strong positive charge make it a useful adsorbent for contaminants in water. The unique properties of PEI make it versatile for various applications, including adsorption of heavy metals and pollutants, thermochromic materials, membranes for multifunctional adsorption, nanofiber sheets for the removal of arsenate, and bio sorbents for the removal of uranyl-carbonate compounds from water. PEI is also useful in improving the fire safety and mechanical properties of epoxy resins (Nan et al. 2023, Elsawy et al. 2022, M. Liu et al. 2022, Z. Lin et al. 2021, Shi et al. 2022).

Polyethylenimine (PEI) has been utilized in various methods for the removal of perfluorinated compounds (PFCs), including perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), from water. A dual grafted fluorinated hydrocarbon amine weak anion exchange resin polymer (FGA-WAEP) was synthesized, in which PEI was used as a grafting agent, and it was used for the adsorption of PFOA from water (Xie et al. 2022). Graphene oxide membranes were modified with PEI to enhance the permselective separation of PFOS from water (Meragawi et al. 2020). Polyacrylonitrile fiber functionalized with fluorous hyperbranched

polyethylenimine (HPFPEI-PAN) was used to selectively remove PFOS in firefighting wastewaters (P. Chen et al. 2021). In addition to adsorption, PEI has also been used for the destruction of PFCs. For instance, PEI was employed in a novel membrane system for the removal and destruction of PFAS (S. Das & Ronen, 2022). Furthermore, the efficacy of surfactants and surface aspects in sequestering PFAS was investigated, and PEI-modified carbon nanotubes were used to adsorb PFAS (Kancharla et al., 2022). (Ateia et al. 2018) reports that poly(ethylenimine)-functionalized cellulose microcrystals (PEI-f-CMC) that showed a near-instant and high removal of PFAS under concentrations relevant to their actual occurrence in the natural environment (i.e.,1000ng/L). The strong positive charge and high degree of protonation of PEI make it effective for the removal and destruction of PFCs, highlighting its potential for use in water treatment applications.

Chapter 3: Material and Methods

3.1 Material

3.1.1 Raw material

Chitosan (viscosity 200-600mPa.s), Epicholohydrin (ECH, purity >99%), PEI (polyethyenimine; CAS No. 9002-98-6), and Pentadecafluorooctanoic acid (PFOA, $C_8HF_{15}O_2$, purity>98%, molecular weight = 414.07 g mol^{-1}) were purchased from Tokyo Chemical Industry (TCI, Japan). Montmorillonite K10 (MMT), N,N-Dimethylacetamide (DMA), Heptadecafluorooctanesulfonic acid potassium salt (PFOS, $CF_3(CF_2)_7SO_3K$, purity>98%, molecular weight = 538.22 g mol^{-1}), Potassium nonafluoro-1-butanesulfonate (PFBS, $CF_3(CF_2)_3SO_3K$, purity>98%, molecular weight = 338.19 g mol^{-1}) and Heptafluorobutyric acid (PFBA, $CF_3CF_2CF_2COOH$, purity>98%, molecular weight = 214.04 g mol^{-1}) were procured from Sigma-Aldrich. The above-mentioned authentic standards of PFOA, PFOS, PFBA and PFBS were used for preparing stock solution of PFAS components at 1g L^{-1}. Granular activated carbon (GAC) (20-40 mesh size) were bought from Duksan company in Korea.

3.2 Methods

3.2.1 Preparation montmorillonite grafted chitosan beads

The process commenced by preparing the chitosan solution, which involved dissolving 1wt% chitosan powder in a 2% (v/v) acetic acid solution, followed by the addition of 5wt% montmorillonite to the chitosan solution. To ensure controlled bead formation, the resulting solution was meticulously

added drop by drop using a peristaltic pump, set at a flow rate of 200 µl min-1, into a 0.5M NaOH solution. This gradual addition facilitated the formation of MT-CB beads, which were allowed to settle and rest for a duration of 3 hours. In order to remove any residual NaOH, the MT-CB beads underwent a thorough washing process with deionized water until a neutral pH of 7.5 was achieved, ensuring the removal of any potential contaminants. Moving forward, the MT-CB beads were subjected to grafting by employing a solution of polyethyleneimine (PEI) dissolved in N, N-dimethyl acetamide (DMA). Specifically, 30g of wet beads were mixed with 30g (ml) of PEI solution in 200 ml of DMA, and the mixture was stirred at a constant rate of 180 rpm for a period of 24 hours, maintaining a temperature of 30ºC. Subsequently, the beads underwent a crosslinking process by immersing them in a 1% (v/v) solution of epichlorohydrin (ECH) in DMA for a duration of 6 hours, while maintaining a temperature of 60ºC. To eliminate any remaining chemicals or impurities, the beads were subjected to additional washing with deionized water. Finally, the beads were carefully vacuum-dried at a temperature of 60ºC

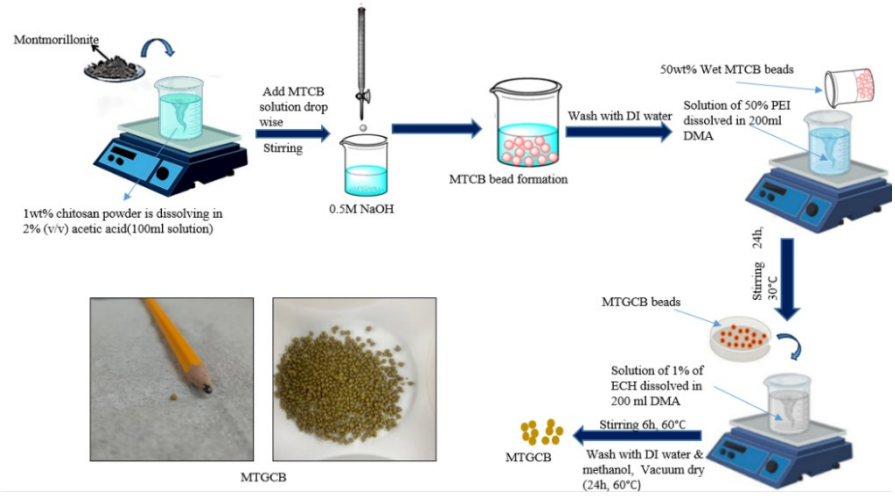

Figure 3.1 Preparation of montmorillonite grafted chitosan beads

for a duration of 24 hours, resulting in the production of modified chitosan beads with enhanced properties suitable for various applications.

3.2.2 Characterization of adsorbent

To examine the characteristics of the MTGCB adsorbent, various analytical techniques were employed. Scanning electron microscopy (SEM) was utilized to observe the morphology of the particles, while an energy dispersive spectroscopy (EDS) microanalysis system was used for elemental composition analysis. Additionally, the Thermo-Scientific Flash 2000 elemental analyzer was employed to quantify the major elemental contents (carbon, oxygen, hydrogen, nitrogen, and sulfur) of the MTGCB particles. Surface oxygen-containing functional groups were investigated using Fourier-transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS). The FT-IR spectra in the range of 4000–400 cm^{-1} were obtained using the Nicolet 6700 instrument from Thermo Scientific (USA), while the XPS spectra were acquired using the ESCAII instrument from AXIS SUPRA (Kratos, UK).

3.2.3 Adsorbate solution

To prepare a stock solution of PFAS substances (PFOA, PFOS, PFBA, and PFBS), an authentic solid standard of each substance was dissolved in 100% methanol. The concentration of each PFAS substance in the stock solution was 1 g L^{-1}. This stock solution was then further diluted to obtain working concentrations as needed, using an appropriate amount of deionized (DI) water.

3.2.3 Batch adsorption tests

Adsorption batch experiments were conducted by adding certain amount of adsorbent into 50 ml polypropylene centrifuge tubes containing

45ml of adsorbate solution at pH 6.5 ± 0.2. The adsorption capacity of each sorbent was determined by preparing multi solutes of PFAS substances (PFOA, PFOS, PFBA, and PFBS) at initial concentrations ranging from 0.05-1 mg L^{-1} for 24h by loading 70 mg L^{-1} of sorbent dosage.

In the kinetic experiments, each data point was determined using an individual batch experiment for the contact times ranging 5 min to 48 h at initial concentration of 0.1 mg L^{-1} of PFAS mixture solution with sorbent dosage of 70 mg L^{-1}

All samples were mechanically agitated at ambient laboratory room temperature (22 ± 2 °C) rotary shaker at 150rpm. and after certain agitation time, samples were centrifuged at 3900 rpm for 20 min and then filtered (pore size 0.2 µm). and the supernatants were kept at refrigerator for further analysis. All experiments were run in triplicates. and the mean value has been reported as the final results. The adsorption procedures, as well as selecting the adsorbent dosages have been conducted following the methods as described by other previous researchers (Feng et al. 2016, Wang et al. 2018, L. Xiao et al. 2017)

3.2.3 Uniform contamination of soil

The soil selected for PFAS stabilization underwent a meticulous process using the MTGCB and GAC method. Classified as SM (silty clay), the soil was sieved to remove particles larger than 4.75 mm, focusing on the fine fraction for subsequent experiments. The detailed particle size distribution of the soil can be observed in Figure 3.2. The specific gravity, pH and organic content of soil were 2.65, 6.65 and 0.59 % respectively. A 10-µg mL^{-1} concentration PFAS solution was prepared to contaminate the soil, ensuring consistency and accuracy throughout.

Next, 500 grams of dried soil were thoroughly mixed with 500 ml of the PFAS solution, aiming for a uniform distribution of PFAS within the soil sample. The mixture was continuously shaken on a shaker for 48 hours to facilitate homogeneity. Subsequently, the mixture was left to naturally dry for two weeks, allowing the soil to absorb the PFAS solution and facilitate stabilization within the soil matrix. This drying period also aided in removing excess moisture, enabling better preservation and storage of the contaminated soil samples.To maintain the stability and integrity of the contaminated soils, they were stored in air-tight containers at a temperature of 4 °C. This storage condition ensured minimal degradation or loss of PFAS compounds, providing a controlled environment for maintaining concentration levels. By following the established research methodology of Sörengård et al. in 2019, the researchers ensured consistency and comparability with prior studies, contributing to a comprehensive understanding of PFAS stabilization techniques.

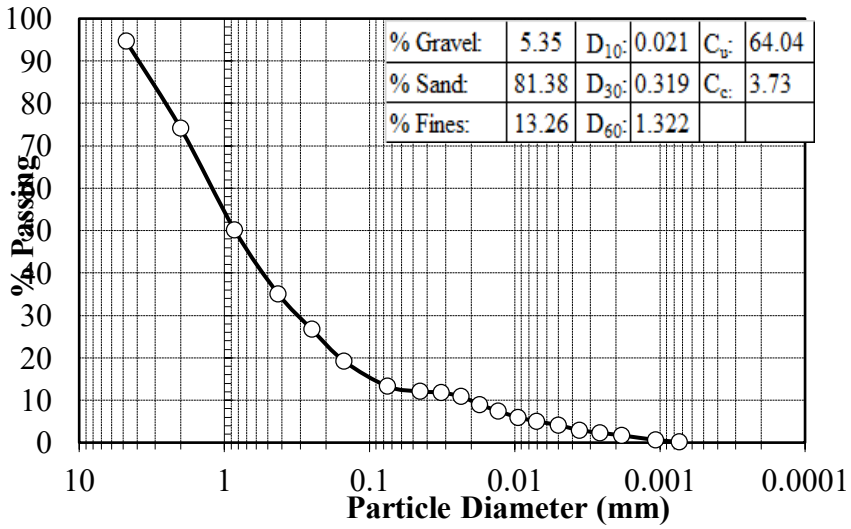

Figure 3.2 Grain size distribution of SM soil

3.2.4 Leaching test

In order to stabilize the contaminated soil, different percentages (2.5%, 5%, and 10%) of two adsorbents, MTGCB and GAC, were added to the soil. The soil-adsorbent mixtures were prepared by adding 2 grams of each sample to 50 ml conical tubes, followed by the addition of 40 ml of deionized water to achieve a liquid-to-soil ratio (L/S) of 20. The samples were then subjected to shaking in an end-over-end shaker at 200 rpm for 7 days, as per the methodologies described in studies conducted by Kabiri et al. (2021) and Sörengård et al. (2019). Control samples consisting of soil without any adsorbent were prepared in a similar manner. After shaking, the samples were centrifuged at 6000 rpm for 20 minutes, and the resulting supernatant was collected for PFAS concentration analysis.

3.2.5 PFAS measurement

Upon completion of each sorption or leaching experiment, the supernatant of each sample was subjected to filtration using a 0.25 polyethersulfone (PES) membrane. This filtration process aimed to remove any particulate matter and ensure a clean supernatant for further analysis. Subsequently, 1ml of the filtered supernatant was prepared to measure the concentration of PFAS. The PFAS concentration analysis was conducted using liquid chromatography-tandem mass spectrometry (LC-MS/MS) equipped with an XDB-C18 guard column, which provided accurate and reliable detection of PFAS compounds.

3.2.6 Geotechnical test

3.2.6.1 Harvard miniature compaction test

Adsorbent was added to the soil in a proportion of 2%, 5% and 10% the total weight in the soil blank, then the compaction test was performed following the ASTM STP38484S.

3.2.6.2 Direct shear test

The direct shear test was performed to evaluate the strength parameter of soil-adsorbent mixtures. The test was performed following the ASTM D 3080 method. The mixture was compacted with 95% of maximum dry unit weight at optimum water content determined previously in the compaction test.

3.2.7 Data analysis

The sorption capacities of each sorbent at any certain time, and under equilibrium conditions have been determined by equation (3.1) and (3.2) respectively.

$$q_t = \frac{(C_i - C_t)V}{m} \tag{3.1}$$

$$q_e = \frac{(C_i - C_e)V}{m} \tag{3.2}$$

Where, q_t (μg g^{-1}) and q_e (mg g^{-1}) are the adsorption capacities at any certain time, and under equilibrium phase, respectively. V (L) is the volume of adsorbate, and m (g) is the dry mass of sorbent. Additionally, C_i (mg L^{-1} or μg

L^{-1}), C_t (μg L^{-1}) and C_e (mg L^{-1}) are the concentrations at initial, any certain time and equilibrium phase of the adsorbate, respectively.

The removal rate of each sorbent was calculated as shown in equation (3.3):

$$R = \frac{(C_i - C_e)}{C_i} \tag{3.3}$$

Where R (%) is the removal rate of each adsorbent

The isotherm adsorption data were analyzed by Langmuir and Freundlich models. Moreover, for describing the mass transfer from solute to the solid sorbent, the kinetics results were analyzed with pseudo-first-order (PFO) and pseudo- second-order (PSO) models. Details about these models are as follows.

The Langmuir model is expressed as:

$$\frac{1}{q_t} = \left(\frac{1}{K_L q_{max}}\right)\frac{1}{C_e} + \frac{1}{q_{max}} \tag{3.4}$$

where q_t (mg g^{-1}) is the amount of adsorbate that is adsorbed on to the solid, C_e (mg L^{-1}) is the solute concentration at equilibrium, q_{max} (mg g^{-1}) is the maximum monolayer capacity of the adsorbent, and K_L (l mg^{-1}) is the Langmuire adsorption constant, which is related to the affinity of adsorption. Note that the both empirical coefficient of q_{max} and K_L can be obtained by plotting $\frac{1}{q_t}$ vs $\frac{1}{C_e}$.

Freundlich model:

$$q_t = K_F C_e^{\frac{1}{n}} \tag{3.5}$$

where q_t and C_e have same definition as equation 3.4, K_F (mg g^{-1}) is the Freundlich adsorption isotherm coefficient, and n is the Freundlich exponent which is related to the intensity of adsorption.

PFO model:

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1 t}{2.303} \quad (3.6)$$

PSO model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3.7)$$

where q_t (mg g^{-1}) is the amount of adsorption at time t, q_e (mg g^{-1}) is the equilibrium adsorption capacity obtained by PFO and PSO models, k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the adsorption constant of PFO and PSO models respectively.

The percentage of each PFAS leached is calculated as follows:

$$\text{Leached PFAS (\% of total)} = \frac{M_{leached}}{M_{total}} \times 100 \quad (3.8)$$

where M_{total} is the concentration of individual PFAS in soil in (µg kg^{-1}). $M_{leached}$ is the mass of leached PFAS and is calculated using equation 3.9

$$M_{leached} = \frac{CV}{m} \quad (3.9)$$

Where C (µg l^{-1}) is the concentration of an individual PFAS in the leachate, V (L) is the volume of leachate and m (kg) is the weight of soil used in leaching experiment.

Chapter 4: Result and Discussion

4.1 Characterization of adsorbent

4.1.1 Element analysis, EDS and SEM

The elemental composition analysis of MTGCB is presented in Table 4.1, revealing the presence of nitrogen. The higher carbon content further confirms the presence of chitosan, as indicated in studies by Ma et al. (2003) and Aguzzi et al. (2014). Additionally, the grafting of PEI contributes to an increased percentage of nitrogen, as reported by Lu et al. (2020). Figure 4.1, displaying the EDS analysis spectrum of MTGCB, also demonstrates the presence of nitrogen. Moreover, the EDS analysis reveals the presence of silicon (Si), aluminum (Al), and magnesium (Mg), indicating the presence of montmorillonite in the adsorbent, as discussed by Bensalem et al. (2017).

Table 4.1 Elemental analyzes of MTGCB

Element	Weight %
Carbon	24.25
Nitrogen	8.68
Oxygen	15.71
Hydrogen	5.73

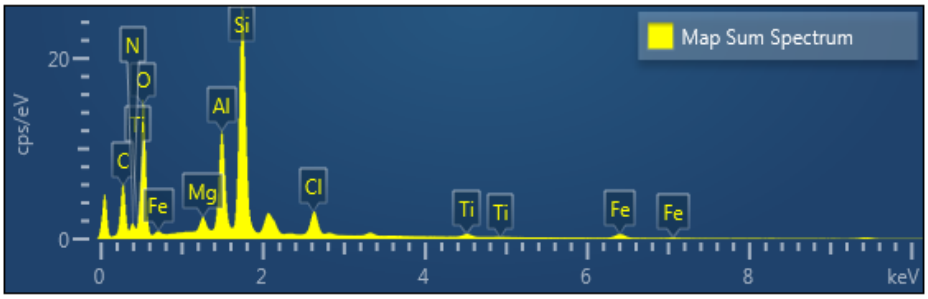

Figure 4.1 EDS spectrum of MTGCB

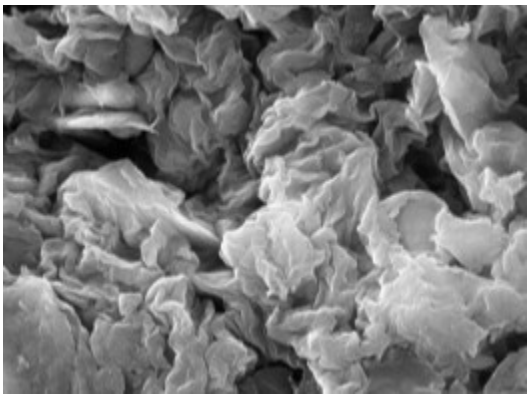

Figure 4.2 SEM image of MTGCB

4.1.2 FTIR analysis

FTIR analysis was conducted to investigate the functional groups present in MTGCB and Montmorillonite (MT). In the case of MT, four characteristic peaks were observed. The peak at 3623 cm^{-1} indicated the presence of O-H stretching vibration, as reported in studies by Bensalem et al. 2021, Liu et al. 2016, and Nesic et al. 2012). The peak at 1630 cm^{-1} corresponded to O-H bending vibration, while the peak at 1031 cm^{-1} indicated the stretching vibration of Si-O, as discussed by Kang et al. 2018, Zabihi et al. 2017 and Nesic et al. 2012). Additionally, the peak at 798 cm^{-1} corresponded to the bending vibration of Si-O, as reported by Yin et al. (2022).

The FTIR analysis of MTGCB revealed several distinctive peaks. The peak at 3304 cm^{-1} was attributed to the coexistence of O-H and N-H stretching vibrations in the secondary amine, indicating the presence of chitosan, as mentioned by G. Wang et al. (2020), Zhao et al. (2020), and Z. Wang et al. (2021). Moreover, the appearance of a broader and more intense peak indicated an increased number of N-H groups in chitosan after PEI grafting, as observed by Chatterjee et al. (2011). The peaks at 2835 cm^{-1} and 2925 cm^{-}

^{1} represented the C-H stretching vibrations in CH_2 and CH_3, respectively, confirming the presence of chitosan, as reported by Bensalem et al. (2017), Nesic et al. (2012), Zabihi et al. (2017), and Han et al. (2022). The peak at 1648 cm^{-1} indicated O-H bending and stretching vibrations of amide group carbonyl bonds C=O, as discussed by Kang et al. (2018) and Zhao et al. (2020). The shift of amide and amine groups could be attributed to the electrostatic interaction between these groups and the negatively charged sites in the clay structure, confirming the complexation between chitosan and MMT, as noted by Nesic et al. (2012), and also due to PEI grafting to chitosan, as observed by Chatterjee et al. (2011). The peak at 1452 cm^{-1} corresponded to the stretching vibration of C-N, indicating the presence of chitosan and PEI in MTGCB, as reported by Han et al. (2022) and Chatterjee et al. (2011). Additionally, the bending vibration of C-H in CH_2 was indicated by this peak, suggesting the presence of chitosan, as discussed by Chatterjee et al. (2011), G. Wang et al. (2020), and W. Wang et al. (2023). The peak at 1371 cm^{-1} was attributed to the $-CH_3$ stretching vibration in amide functional groups, indicating the presence of chitosan, as documented by Wang et al. (2020) and W. Wang et al. (2023). Finally, the peak at 1006 cm^{-1} corresponded to the Si-O and C-O stretching vibrations, and the decrease in intensity of the Si-O bond compared to MT was attributed to the overlap of the C-O bond of chitosan, confirming the impregnation of chitosan in MT, as reported by Bensalem et al. (2021) and Liu et al. (2016).

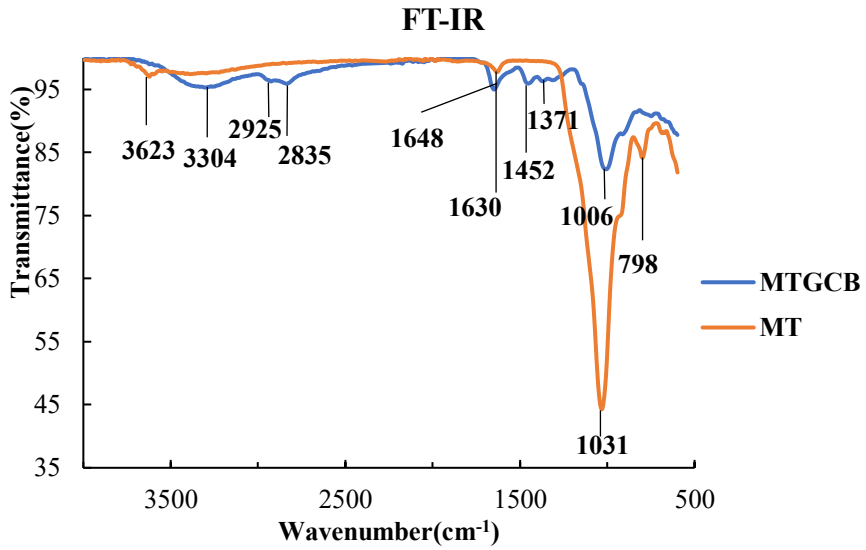

Figure 4.3 FTIR analysis of MT and MTGCB

4.1.3 XPS analysis

XPS analysis was conducted to analyze the dominant peaks observed in montmorillonite (MT). The results revealed specific peaks at different binding energies, including Al2p (73.5 eV), Si2p (102.5 eV), Al2s (118.5 eV), Si2s (154.5 eV), C1s (284.69 eV), N1s (400.99 eV), and O1s (531.99 eV), as demonstrated in Figure 4.4 (a) (Bensalem et al. 2021, Ye et al. 2021). Furthermore, a more detailed examination of the O1s and C1s peaks in MT provided additional insights. Figure 4.4 (b) and (c) display the deconvoluted spectra of O1s and C1s, respectively. Within the C1s spectrum, distinctive peaks were observed at 284.36 eV, 285.37 eV, 286.71 eV, and 289.04 eV, corresponding to C-H/C-C, C-O/C-OH, O-C-O, and O-C=O, as reported in various studies (Bensalem et al. 2021, Kaur et al. 2018, Bensalem et al. 2017, Cheng et al. 2022). Similarly, the O1s spectrum exhibited three distinct peaks at 530.50 eV, 531.89 eV, and 533.48 eV, representing Al-OH, Si-O, and O-H

in adsorbed water respectively, as discussed in the literature (Cheng et al. 2022, Guo et al. 2022, Y. Wang et al. 2022, Tran et al. 2005).

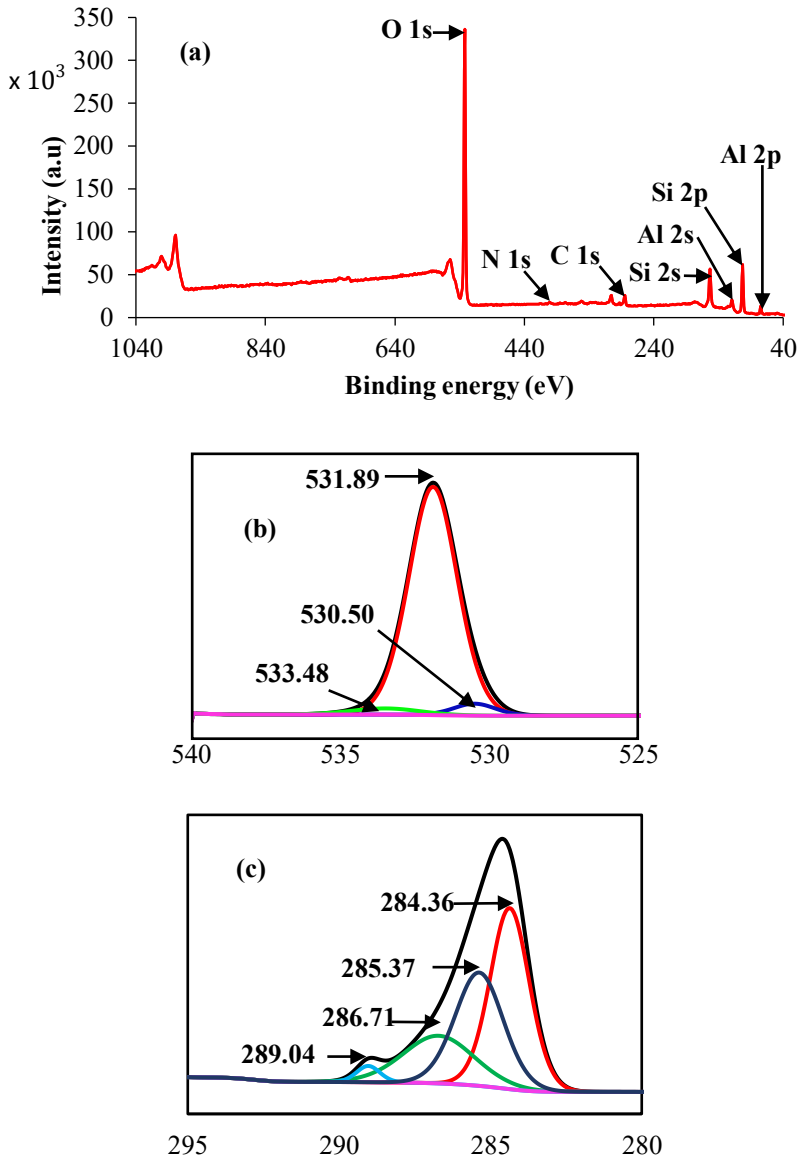

Figure 4.4 (a) XPS survey spectrum (b) O1s spin-orbit peaks
(c) C1s spin-orbital peaks of MT

The X-ray photoelectron spectroscopy (XPS) analysis of MTGCB yielded significant findings regarding its spectral features. The observed

spectrum exhibited a broad peak encompassing multiple peaks associated with distinct binding energies, namely Al2p (74 eV), Si2p (102 eV), Al2s (118.5 eV), Si2s (154 eV), C1s (284.80 eV), N1s (398.90 eV), and O1s (531.30 eV) (Figure 4.5 (a)). The presence of Al2p, Si2p, Al2s, and Si2s peaks signifies the presence of montmorillonite (MT), while the heightened intensities of N1s and C1s peaks indicate the inclusion of chitosan within MTGCB (Ye et al. 2021, Bensalem et al. 2021). Regarding the O1s spectrum, it underwent deconvolution, leading to the identification of distinct peaks at 531.35 eV, 532.10 eV, and 532.81 eV. The peak at 531.36 eV corresponds to the presence of O-H/C=O moieties, which are characteristic of chitosan (Ye et al. 2021, Liu et al. 2016, W. Wang et al. 2023, Zeng et al. 2019, Won et al. 2014). The peak at 532.10 eV can be attributed to Si-O bonds derived from MT, while the peak at 532.81 eV indicates the presence of chitosan through C-O bonds (Liu et al. 2016, Won et al. 2014, Yin et al. 2022).Additionally, the emergence of a peak at 398.82 eV implies the grafting of polyethyleneimine (PEI) onto chitosan, corresponding to tertiary amine bonds (-N<) (Z. Wang et al. 2021, Zhao et al. 2020, Lu et al. 2020). The peak at 399.98 eV indicates the existence of -NH_2/–NH groups, confirming the presence of chitosan and PEI (Liu et al. 2016, G. Wang et al. 2020, C. Xiao et al. 2017, Won et al. 2014). Furthermore, a novel peak at 401.49 eV signifies the presence of -NH3+ species, indicating robust interactions with negatively charged sites in both MMT and chitosan. Notably, the intensity of -NH_3^+ increases upon PEI grafting onto chitosan, aligning with the results obtained from Fourier-transform infrared (FTIR) analysis(Lu et al. 2020, Kang et al. 2018, Zhao et al. 2020).In the C1s spectrum, three distinct peaks at 284.52 eV, 285.74 eV, and 287.64 eV correspond to (C-C/C-H), (C-N/C-OH/C-O), and C=O, respectively, indicating the presence of various carbon-based functional groups (Bensalem et al. 2021, Fan et al. 2021).

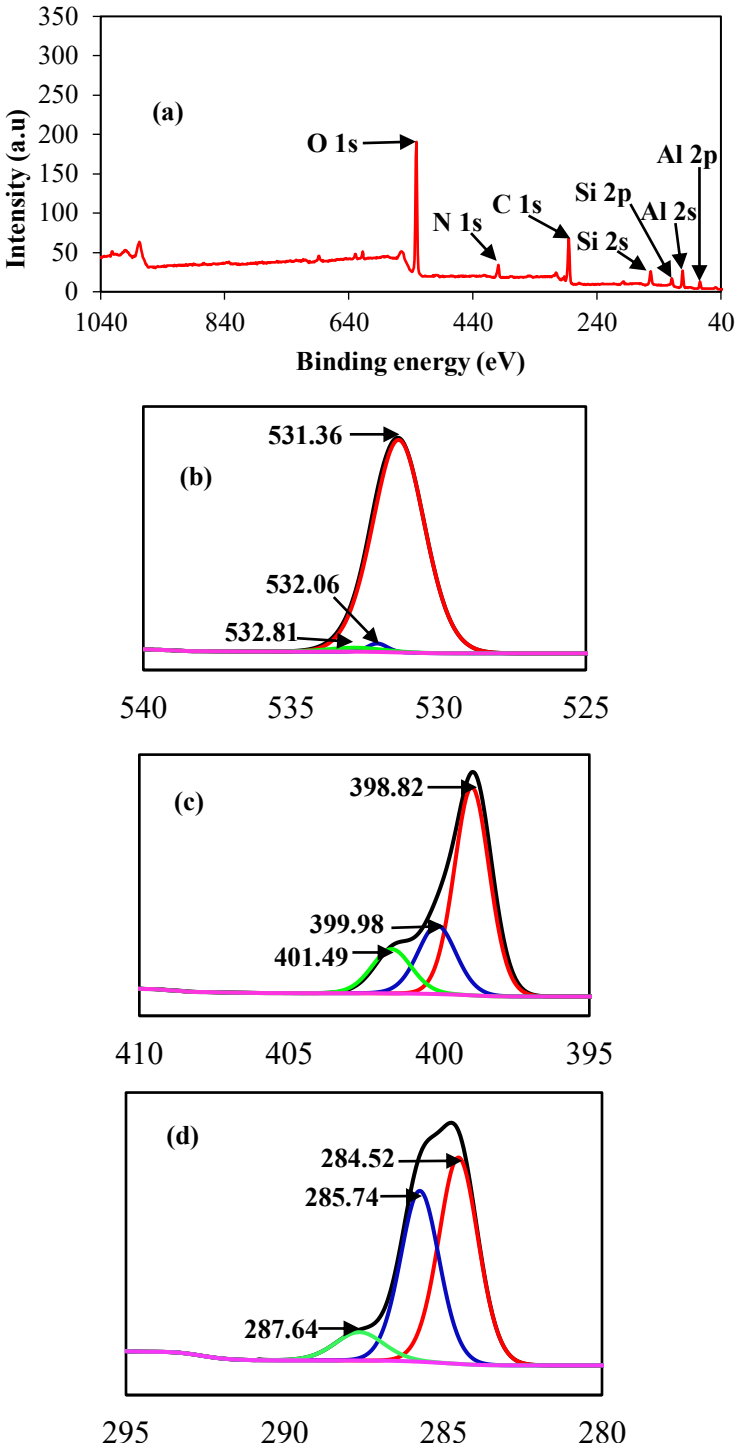

Figure 4.5 (a) XPS survey spectrum (b) O1s spin-orbit peaks (c) N1s spin-orbit peaks (d) C1s spin-orbital peaks of MTGCB

4.2 Batch adsorption test

4.2.1 Isotherm adsorption test

The removal rates of PFAS within a multi-solute system. Specifically, the compounds under examination were PFBA, PFBS, PFOA, and PFOS. Two distinct materials, MTGCB and GAC, were employed to assess the removal efficiency of these PFAS compounds. The obtained results, as illustrated in Figure 4.6, revealed noteworthy patterns in the removal rates with respect to the chain lengths of the PFAS compounds.

The data indicated that longer-chain PFAS compounds exhibited higher removal rates compared to their shorter-chain counterparts, regardless of the adsorbent material employed. This finding suggests that the chain length plays a significant role in the removal process. Furthermore, the removal efficiency followed a specific sequence: PFOS > PFOA > PFBS > PFBA. This order implies that PFOS, with the longest chain length, demonstrated the highest removal efficiency, while PFBA, possessing the shortest chain length, exhibited the lowest removal efficiency. The less effective removal of short-chain PFAS is attributed to their weaker hydrophobicity of short-chain PFAS (F. Li et al. 2020).

Additionally, it was observed that the removal efficiency of PFSA compounds exceeded that of PFCA compounds with equivalent chain lengths. This observation suggests that the functional group attached to the PFAS compounds significantly influences their removal efficiency. The presence of the sulfonate group in PFSA compounds may enhance their interaction with the adsorbents, leading to improved removal efficiency. Conversely, the carboxylate group in PFCA compounds might exhibit weaker adsorption

interactions, resulting in relatively lower removal efficiency. Both trends have been reported in previous studies (Ateia et al. 2018, Li et al. 2023).

The GAC demonstrated a superior removal rate for long-chain PFAS, achieving a removal rate of over 95% regardless of the initial concentration. However, as the initial concentration increased, the removal rate for short-chain PFAS, such as PFBA and PFBS, decreased from 92% to 7% and 97% to 62% respectively. This decrease in removal rate for short-chain PFAS at higher concentrations can be attributed to the saturation of adsorption sites, where the availability of adsorption sites becomes limited, favoring the adsorption of long-chain PFAS over short-chain PFAS since long chain are more hydrophobic (W. Wang et al. 2019, Maimaiti, et al. 2019).The adsorption mechanism of GAC relies on hydrophobicity, which explains the higher removal rate for long-chain PFAS compared to short-chain PFAS (Saeidi et al. 2021, Park et al. 2020) and there might be formation of hemi micelle of long chain at higher concentration too (Deng et al., 2012).

In the case of MTGCB, a similar high removal rate of over 95% was observed for long-chain PFAS. Interestingly, as the initial concentration increased, the removal rate for short-chain PFAS, such as PFBA and PFBS, showed an increase from 33% to 53% and 74% to 92% respectively. This can be attributed to the unique properties of MTGCB, which combines hydrophobicity and positive charge due to the presence of chitosan and PEI (Zhang et al. 2011, Lei et al. 2023, Ateia et al., 2018, Kebria et al. 2023). The higher electrostatic affinity of short-chain PFAS compared to long-chain PFAS may explain why the short-chain compounds are not readily replaced by the long-chain ones (Parker et al. 2022). The increase in removal rate with increasing concentration may be attributed to the replacement of long-chain PFAS by short-chain PFAS on electrostatic sites. Additionally, at higher

concentrations, the formation of hemi micelles composed of long-chain PFAS could also contribute to the observed phenomenon (Q. Zhang et al., 2011).

The adsorption capacity of GAC and MTGCB for different PFASs was determined using the Freundlich and Langmuir models, as shown in Table 4.2. Both adsorbents showed an increase in capacity as the concentration of PFASs increased. The isotherm data for GAC indicated a better fit with the Langmuir and Freundlich model, suggesting there can be mono and multi-layer adsorption. This finding is consistent with previous studies (Cantoni et al. 2021, Saeidi et al., 2020). The maximum adsorption capacities for PFBA, PFBS, PFOA, and PFOS were 2.38 mg/g, 6.22 mg/g, 10.71 mg/g, and 10.94 mg/g, respectively. It can be observed that the adsorption capacity increased from short to long-chain PFASs, supporting the notion that GAC exhibits higher adsorption for more hydrophobic PFASs.

MTGCB exhibits adsorption behavior that conforms to both the Langmuir and Freundlich models, suggesting both monolayer and multi-layer adsorption (Kebria et al., 2023). The increased concentration of PFAS compounds enhances the likelihood of multi-layer adsorption, further supporting this observation. The maximum adsorption capacities according to the Langmuir model for PFBA, PFBS, PFOA, and PFOS were 3.09 mg/g, 6.52 mg/g, 10.52 mg/g, and 12.10 mg/g, respectively. The increase in adsorption capacity for PFBS and PFOA with GAC can be attributed to its high surface area (Wu et al., 2020; Y. Wang et al., 2015). In contrast, MTGCB exhibited higher capacity for PFOS and PFBA due to the combined effects of hydrophobicity and electrostatic interactions, especially pronounced for PFOS, while the lesser hydrophobicity of PFBA led to greater adsorption through electrostatic interactions (Pauletto and Rodríguez-Castellón, 2022; Huang et al., 2018.

Table 4.2 Langmuir and Freundlich parameters for PFAS substance sorption by GAC & MTGCB

PFAS	Adsorbent	Langmuir model			Freundlich model		
		q_{max} (mg g^{-1})	K_L (L mg^{-1})	R^2	K_F (mg g^{-1})x (mg L^{-1})$^{1/n}$	1/n	R^2
PFBA	GAC	2.38	97.65	0.995	3.35	3.69	0.922
	MTGCB	3.09	2.38	0.965	17.87	0.81	0.990
PFBS	GAC	6.22	229.57	0.952	13.18	2.77	0.953
	MTGCB	6.52	8.51	0.998	695.22	0.61	0.992
PFOA	GAC	10.71	103.66	0.997	89.55	1.54	0.985
	MTGCB	10.52	20.65	0.958	569.86	0.88	0.972
PFOS	GAC	10.94	70.30	0.999	115.98	1.36	0.991
	MTGCB	12.10	68.83	0.998	131.30	1.34	0.990

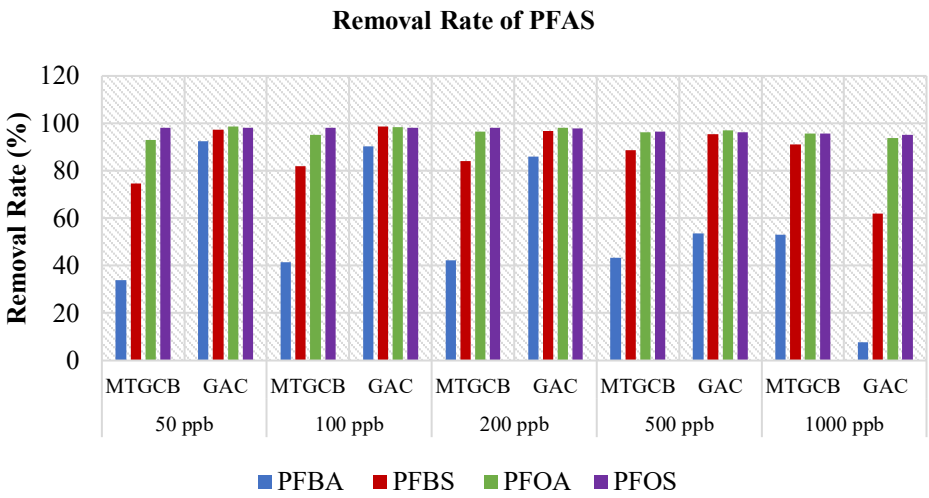

Figure 4.6 Removal rate of PFAS at different concentrations for GAC and MTGCB (pH:6.5, T:22 °C)

4.2.2 Kinetics adsorption test

Figure 4.7 illustrates the adsorption kinetics of GAC and MTGCB for a multi-solute PFAS system. The experimental data demonstrate that both GAC and MTGCB exhibit a gradual increase in adsorption capacity as the contact time is extended until reaching a point of saturation. This behavior is consistent with typical adsorption processes, where initial rapid adsorption is followed by slower uptake until equilibrium is attained. Notably, the adsorption capacity of the investigated PFAS compounds follows a specific order, with PFOS exhibiting the highest capacity, followed by PFOA, PFBS, and PFBA. GAC exhibited higher sorption capacity for all PFAS compared to MTGCB. At low concentrations such as 0.1 mg L^{-1}, the competitive nature among PFAS is reduced, allowing for more available adsorption sites for short-chain compounds. This observation aligns with the results obtained from the isotherm adsorption study.

The analysis of adsorption equilibrium time reveals distinct patterns for GAC and MTGCB. GAC achieves equilibrium for all PFAS compounds within 24 hours, which aligns with previous studies in the field (N. Liu et al., 2021; Deng et al., 2015; D. Zhang et al., 2016). These consistent findings support the reliability of the observed equilibrium time and suggest that GAC exhibits a relatively fast adsorption rate. In contrast, MTGCB demonstrates varying equilibrium times, with most PFAS compounds requiring 48 hours to reach equilibrium, except for PFBA, which achieves equilibrium within 24 hours. The discrepancy in equilibrium times can be attributed to the molecular size and hydrophobicity of the PFAS compounds. Smaller molecules like PFBA have greater mobility and can readily diffuse into the porous structure of the adsorbent, resulting in faster adsorption. On the other hand, PFBA, with its shorter carbon-fluorine (C-F) chain and lower hydrophobicity, relies primarily on electrostatic attraction for adsorption. Other PFAS compounds with higher hydrophobicity facilitate both hydrophobic and electrostatic interactions, potentially leading to the formation of hemi-micelles during the adsorption process. Thus, the complex interactions between PFAS compounds and the adsorbent require more time for rearrangement and establishment of equilibrium (Q. Zhang et al., 2011). Understanding the kinetic profiles of adsorption processes is crucial for designing and operating efficient wastewater treatment systems targeting PFAS removal. These profiles provide valuable information about the adsorption rate, equilibrium time, mass transfer mechanisms, and overall adsorbent efficiency. In addition to key operating conditions such as pH and temperature, particle size and porosity of the adsorbents significantly influence the adsorption kinetics of PFAS compounds. In this context, GAC stands out with its shorter equilibrium time compared to MTGCB. This advantage can be attributed to the well-developed pore structure and high surface area of GAC (Lei et al., 2023).

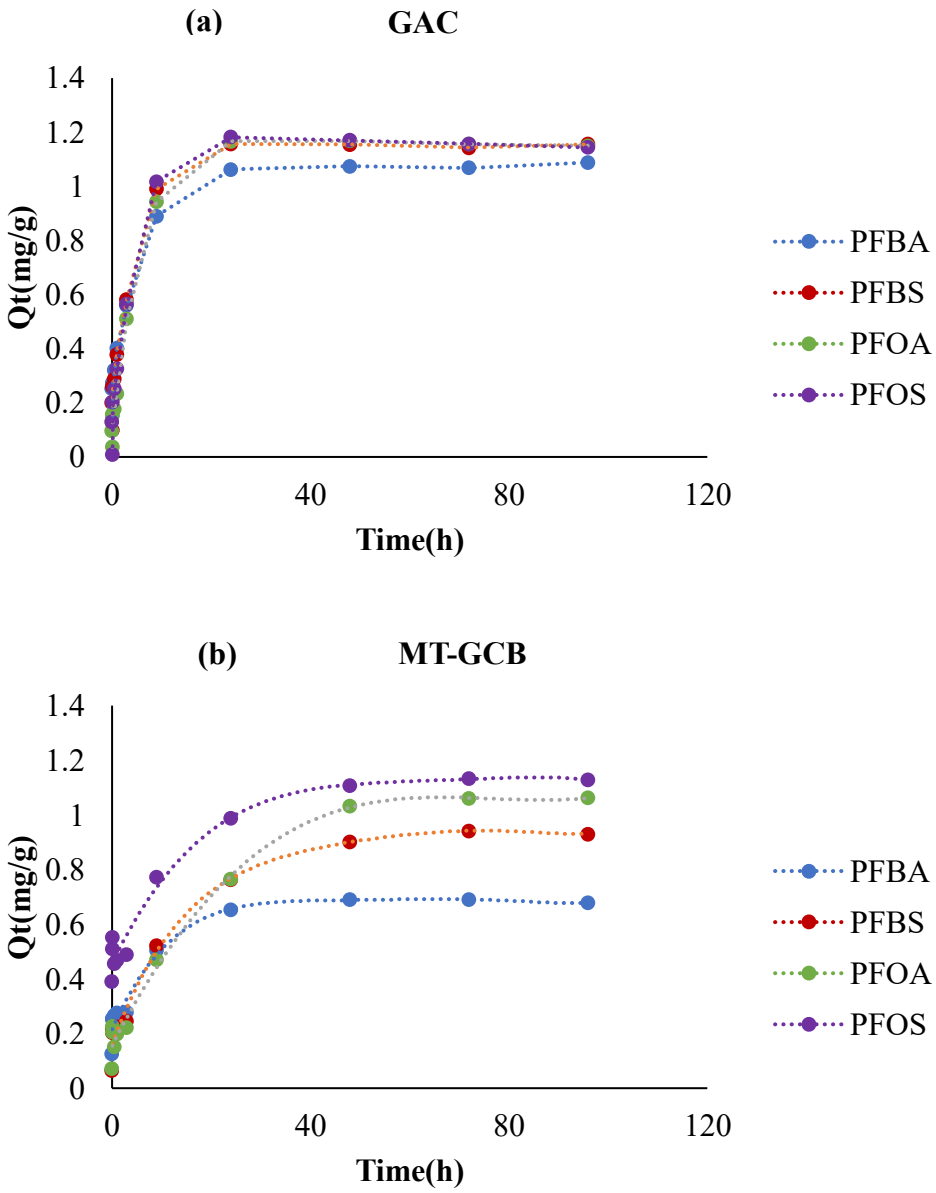

Figure 4.7 (a) Adsorption kinetics of PFAS on GAC (a) Adsorption kinetics of PFAS on MTGCB ((pH:6.5, T:22 °C at 0.1 mg L^{-1})

To comprehensively investigate the kinetics involved in the adsorption process, the obtained experimental data were thoroughly analyzed using two widely used kinetic models: the pseudo-first-order (PFO) and pseudo-second-order (PSO) models. Detailed results for GAC and MTGCB can be found in Table 4.3. Interestingly, both GAC and MTGCB exhibited excellent fitting with the pseudo-second-order kinetics model, confirming the findings of previous studies (Liu et al. 2021, Zhang et al. 2019, Jiang et al. 2022, Yu et al. 2008, Q. Zhang et al. 2011, Elanchezhiyan et al. 2021). The higher values of the fitting coefficient (R^2) obtained from the pseudo-second-order model indicate that the sorption of PFAS by both adsorbents is predominantly influenced by chemical sorption and is directly proportional to the number of active sites available on the sorbent (D. Li et al. 2023, Boyer et al. 2021).

The initial adsorption rates (v_0^a) for GAC were found to be 0.891, 0.916, 0.550, and 0.417 mg g^{-1} hr^{-1} for PFBA, PFBS, PFOA, and PFOS, respectively. On the other hand, for MTGCB, the initial adsorption rates were 0.499, 0.283, 0.208, and 0.842 mg g^{-1} hr^{-1} for PFBA, PFBS, PFOA, and PFOS, respectively. The higher sorption rate of short-chain PFAS in GAC can be attributed to the faster kinetics exhibited by these PFAS due to their small molecular size and high mobility (Maimaiti et al. 2018). In contrast, long-chain PFAS with greater hydrophobicity and larger molecular size tend to form micelles or aggregates, leading to slower diffusion rates and kinetics during sorption (Shih and Wu 2020). For MTGCB, the adsorption rate followed the order of PFOS > PFBA > PFBS > PFOA, the order of adsorption rate for PFAS in MTGCB can be attributed to the diffusion time constant, D/Rad, where D is the diffusivity of the adsorbate and Rad is the radius of the adsorbent. A study by Loganathan and Wilson 2022, have shown that the diffusion coefficient follows the order of PFOS > PFBA > PFBS > PFOA, which matches with the sorption rate order of PFAS by MTGCB. (Li et al. 2023).

Table 4.3 Pseudo-first-order and pseudo-second-order parameters for PFAS sorption by GAC and MTGCB

PFAS	Adsorbent	Pseudo-first-order			Pseudo-second-order			
		K_1 (h^{-1})	q_e (mg g^{-1})	R^2	K_2 (g mg^{-1} h^{-1})	q_e (mg g^{-1})	v_0[a] (mg g^{-1} h^{-1})	R^2
PFBA	GAC	0.060	0.586	0.892	0.740	1.096	0.891	0.994
	MTGCB	0.043	0.350	0.787	1.035	0.695	0.499	0.998
PFBS	GAC	0.060	0.483	0.686	0.667	1.172	0.916	0.999
	MTGCB	0.047	0.702	0.921	0.306	0.963	0.284	0.992
PFOA	GAC	0.054	0.491	0.548	0.390	1.188	0.550	0.998
	MTGCB	0.048	0.956	0.953	0.167	1.119	0.209	0.982
PFOS	GAC	0.040	0.519	0.528	0.290	1.199	0.418	0.990
	MTGCB	0.051	0.615	0.942	0.647	1.141	0.843	0.998

4.3 Leaching test

Figure 4.8 presents the results of the leaching test conducted on soil stabilized with GAC and MTGCB. The findings indicate that the addition of 2% GAC resulted in less than 2% leaching of PFBA, while all other PFAS were effectively stabilized in the soil. These results are consistent with previous studies and can be attributed to the hydrophobic sorption mechanism, which is influenced by the carbon chain length of the PFAS. The limited leaching of PFBA is due to its hydrophobic nature (Barth et al. 2021, Duchesne et al. 2020, W. Zhang and Liang 2022, Sörengård et al. 2019).

In the case of MTGCB, as the percentage of adsorbent increased, the leaching of PFAS from the soil decreased. For 10% MTGCB addition, the leaching percentages were 29.3% for PFBA, 11.7% for PFBS, 10.7% for PFOA, and 0% for PFOS. The leaching order of PFAS in soil with MTGCB addition followed PFBA > PFBS > PFOA > PFOS, which can be attributed to the hydrophobicity and functional groups of the PFAS. PFAS with longer carbon chains and sulfonic functional groups exhibited lower leaching compared to those with shorter chains and carboxylate groups (Sörengård et al. 2019, Cai et al. 2022). While electrostatic and hydrophobic interactions are reported as the dominant mechanisms for PFAS stabilization in soil by sorbents in some studies (Higgins and Luthy 2006, Sörengård et al. 2019, Du et al. 2014), the results obtained with MTGCB suggest that hydrophobicity can be the dominant mechanism in soil. These findings align with other studies that highlight the hydrophobic nature of MTGCB and its relatively higher leaching compared to GAC (Kabiri et al. 2023, Sörengård et al. 2020).

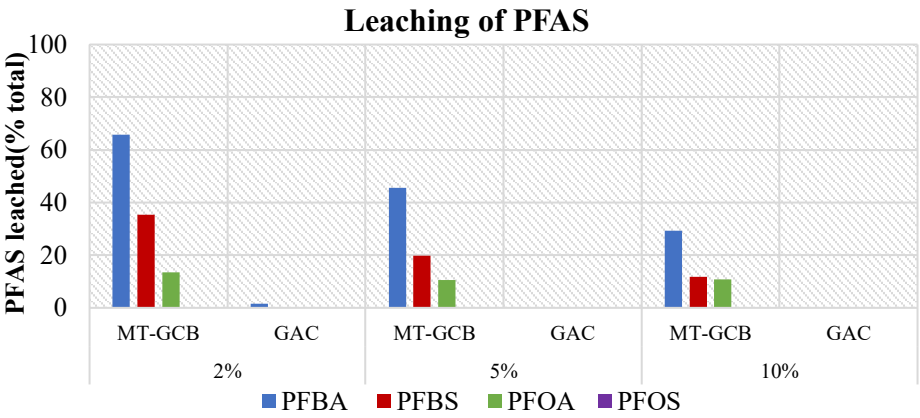

Figure 4.8 ASLP leaching results shown as percentage of PFAS leached from soil treated with GAC and MTGCB at 10 ug/g (pH:7, T:25 °C, L/S :40/2)

4.4 Geotechnical test

4.4.1 Harvard miniature test

Figure 4.9 (a) demonstrates that the addition of GAC or MTGCB to soil results in a decrease in the maximum dry unit weight of the soil. The reduction in maximum dry unit weight is more significant for GAC compared to MTGCB. Specifically, for GAC, the maximum dry unit weight decreased from 1.907 g cm^3 to 1.813 g cm^3 and further to 1.526 g cm^3 for the addition of 2%, 5%, and 10% of the adsorbent, respectively. On the other hand, for MTGCB, the corresponding values were 1.891 g cm^3, 1.860 g cm^3, and 1.748 g cm^3. These findings indicate that the addition of GAC has a greater impact on reducing the maximum dry unit weight of the soil compared to MTGCB.

The decrease in maximum dry density observed in the mixture of adsorbent can be attributed to the difference in specific gravity between the adsorbent and the soil. The specific gravity of the soil is typically around 2.65, while the specific gravity of GAC is 2.1 and MTGCB is 2.5 (Akbarimehr et

al., 2020, Seda et al. 2007). Since the specific gravity of MTGCB is closer to that of the soil, the change in maximum density is relatively smaller in the mixture of MTGCB compared to GAC. This indicates that the presence of MTGCB in the soil has a lesser impact on the overall density of the mixture due to its closer resemblance to the soil's specific gravity.

Figure 4.9 (b) presents the water content at maximum dry unit weight. For GAC, the water content increases to 16.5% with the addition of 5% of the adsorbent and then decreases to 11% for a 10% addition. These values are

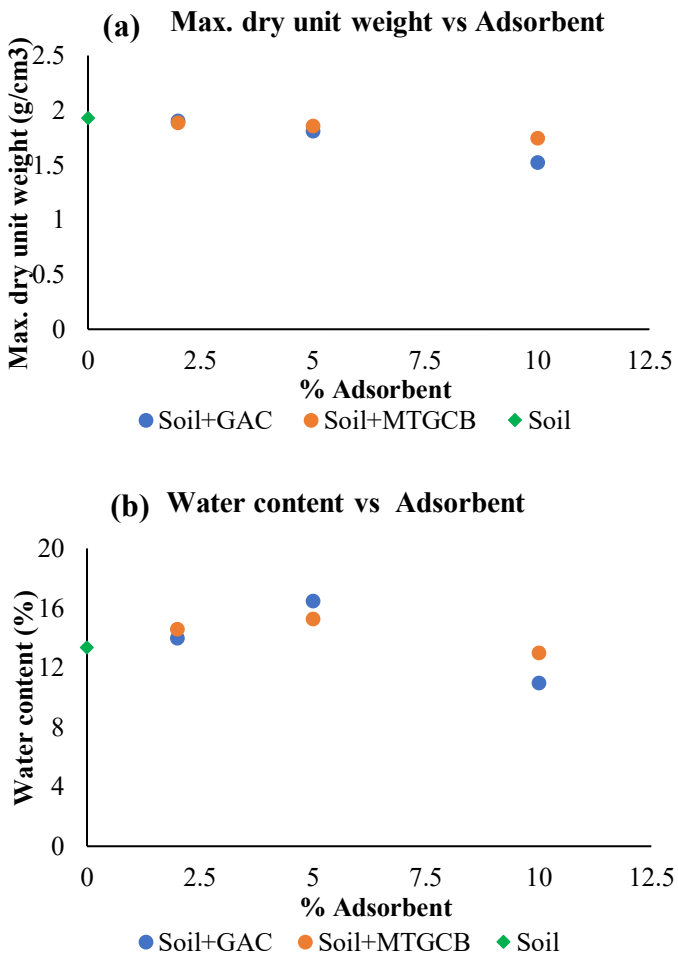

Figure 4.9 (a) Maximum dry unit weight and (b) Water content of, Soil+GAC, Soil+MTGCB and Soil

below the water content of the blank soil. Similarly, for MTGCB, the water content increases to 15% with a 5% addition and remains at 13% with a 10% addition, which is comparable to the water content of the blank soil (13.35%).

The increase in water content observed in the soil mixed with GAC can be attributed to the water holding capacity of GAC. GAC possesses a larger surface area and a porous structure, which allows it to effectively retain water within its pores (Rizhiya et al., 2015, Zamulina et al., 2020).

4.4.2 Direct shear test

The incorporation of GAC and MTGCB into the soil results in an increase in the friction angle, reaching its maximum at a 5% addition and decreasing when the addition is increased to 10%. The maximum friction angles observed were 41.9°, 39.8°, and 36.9° for the soil mixed with GAC, MTGCB, and the blank soil, respectively. Even at a 10% addition of the adsorbent, the friction angle remained higher than that of the blank soil (Figure 4.10 (a). Figure 4.10 (b) presents the variation of cohesion with the addition of adsorbents into the soil. The cohesion increased until a 2.5% addition of GAC and then decreased by 12.6 kPa with a 10% addition. The increase in friction angle and cohesion observed in the soil-GAC mixture can be attributed to the angular shape of GAC particles, which facilitate interlocking between soil particles and GAC, thereby increasing the shear strength of the mixture (Philibert et al., 2020; Prabhakara et al., 2019, Tatlisoz et al., 1998).

Similarly, in the case of MTGCB, the friction angle and cohesion increased until a 5% addition to the soil, after which they decreased to 38.7° and 28.9 kPa, respectively. The presence of montmorillonite in MTGCB enhances the specific surface area of the soil, leading to an increased number of contact points between soil particles and strengthened cohesion (Yuan et al.,

2022). However, when the MTGCB content exceeds the optimal value, the montmorillonite absorbs water and swells, disrupting the original soil structure. This thickens the combined water film, reduces the number of contact points between soil particles, and weakens the cementation between particles, resulting in a decrease in the internal friction angle, cohesive strength, and shear strength (Yuan et al., 2022).

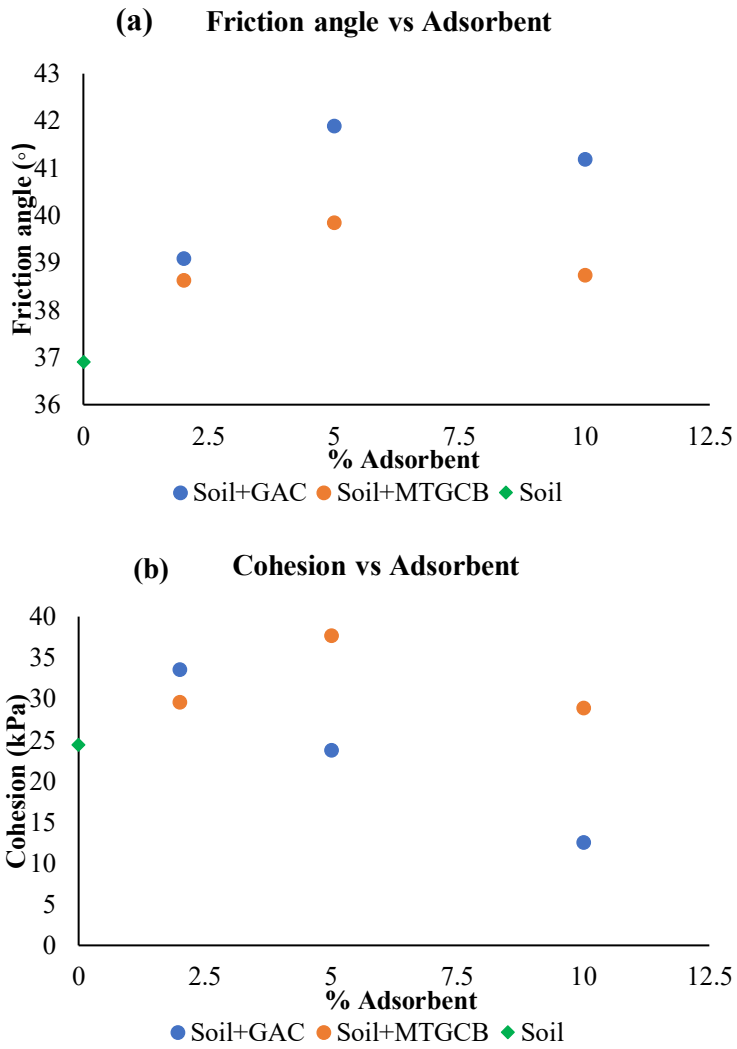

Figure 4.10 (a) Friction angle (b) Cohesion of Soil+GAC, Soil+MTGCB and Soil

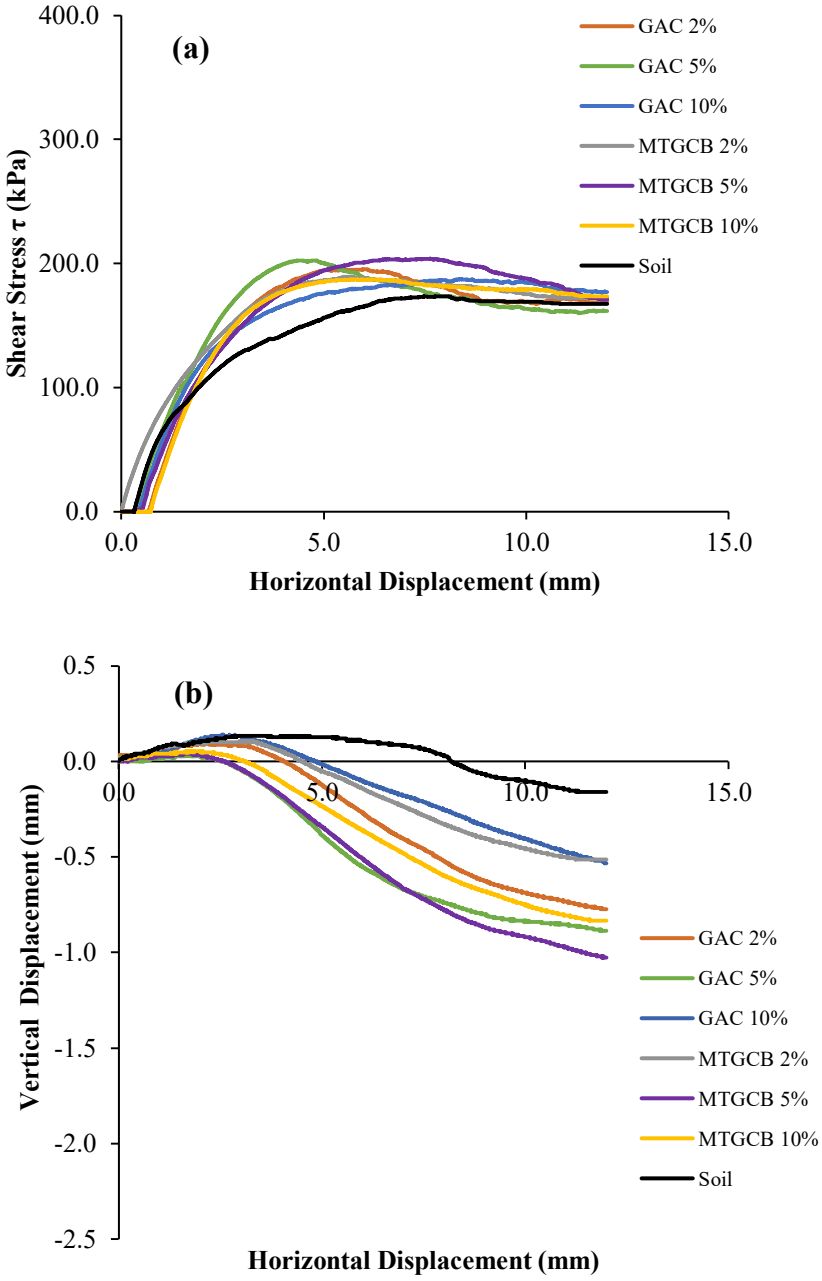

Figure 4.11 (a) Shear stress vs Horizontal displacement (b) Vertical displacement vs Horizontal displacement for soil with different % of adsorbent

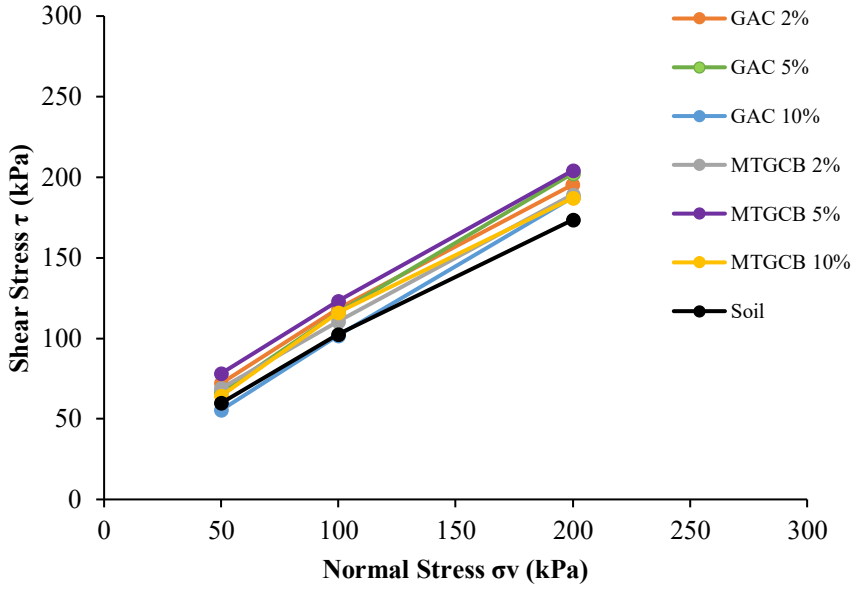

Figure 4.12 Shear stress vs Normal stress for soil with different % of adsorbent

Chapter 5: Conclusions and future studies

5.1 Conclusion

In conclusion, the comprehensive analysis of adsorption tests and leaching behavior of per- and polyfluoroalkyl substances (PFAS) on granular activated carbon (GAC) and montmorillonite grafted chitosan bead (MTGCB) has provided valuable insights for their application in PFAS removal and soil stabilization. The removal efficiency followed the order of PFOS > PFOA > PFBS > PFBA, with short-chain PFAS compounds exhibiting lower removal efficiency due to weaker hydrophobicity. PFSA compounds showed higher removal efficiency than PFCA compounds of the same chain length, attributed to the sulfonate group enhancing interactions with the adsorbents. GAC demonstrated excellent removal rates for long-chain PFAS compounds, while MTGCB showed similar high removal rates and also improved removal of short-chain PFAS compounds at higher concentrations.

Both GAC and MTGCB exhibited increased adsorption capacities with rising PFAS concentrations, with both adsorbents conforming well to the Langmuir and Freundlich model, which indicates there might be combination of mono and multi-layer sorption. MTGCB demonstrated a higher capacity for PFOS, PFBS and PFBA due to hydrophobicity and electrostatic interactions, while for PFOA it is similar to GAC. Equilibrium adsorption was achieved gradually, with GAC reaching equilibrium within 24h for all PFAS compounds, while MTGCB had equilibrium time within 48h except PFBA which is 24h due to its molecular size. Kinetic analysis indicated that both adsorbents followed pseudo-second-order kinetics, with chemical sorption as the primary mechanism. GAC exhibited higher initial adsorption rates for short-chain

PFAS due to molecular size, while MTGCB's sorption rate order was PFOS > PFBA > PFBS > PFOA, influenced by diffusion coefficient.

GAC exhibited excellent stabilization with minimal leaching, while MTGCB demonstrated a decreasing trend in leaching as the percentage of adsorbent increased. Longer carbon chains and sulfonic groups in PFAS contributed to better stabilization. The optimal addition percentage for GAC in soil stabilization was found to be 2%, while for MTGCB, it was 10%.

In the compaction test, the addition of both adsorbents resulted in a decrease in the maximum dry unit weight of the soil due to their low specific gravity and the increased water content in GAC due to presence of its water holding capacity while in MTGCB the variation was negligible. However, in direct shear test the friction angle and cohesion increased with the addition of GAC due to its angular shape and for MTGCB due to the presence of montmorillonite, which helped bind the soil particles together. To achieve improved mechanical properties, an optimal addition percentage of 5% was recommended for GAC, while for MTGCB, 10% was found to be suitable.

In summary, this thesis highlights the potential of MTGCB as a promising alternative to GAC for the stabilization of PFAS in soil. MTGCB demonstrates comparable adsorption performance to GAC, particularly for long-chain PFAS compounds, and exhibits effective leaching control. Additionally, MTGCB enhances the mechanical properties of soil, making it a multifunctional adsorbent for soil remediation applications. The recommended optimal addition percentages of 5% for GAC and 10% for MTGCB can be utilized for achieving soil stabilization and improved mechanical properties. Further research is required to fully explore the potential of MTGCB and its suitability for large-scale implementation in PFAS-contaminated sites.

5.2 Future studies

Further studies could be conducted to deepen the understanding and application of MTGCB as an alternative to GAC for PFAS removal and soil stabilization. Some potential avenues for future research include:

1. Long-term performance assessment: Conducting studies to evaluate the long-term stability and effectiveness of MTGCB in PFAS removal and soil stabilization. Leaching behavior of MTGCB over extended periods of time under various environmental conditions and by column leaching test.

2. Distribution coefficient (K_d): The values of K_d are used to predict the mobility and transport of contaminants through soils. It quantifies the partitioning of contaminants between the solid phase (soil) and the liquid phase (water) and provides insights into their mobility and potential for leaching. Higher K_d values indicate stronger adsorption of contaminants to the soil, resulting in reduced mobility and lower leaching potential.

3. Field-scale applications: Implementing pilot-scale or field-scale studies to assess the performance of MTGCB in real-world PFAS-contaminated sites. This would involve evaluating its effectiveness, practicality, and economic feasibility as compared to traditional GAC-based systems.

4. Permeability: Investigate the impact of adsorbents on the permeability of soil. Permeability determines the rate at which water or other fluids can flow through the soil. It can help to understand if the addition of adsorbents affects the drainage characteristics of the soil and its ability to transport contaminants or nutrients.

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Abstract in Korean

몬모릴로나이트 접목 키토산 비드를 이용한 표면하에서의 PFAS 흡착

초록

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퍼- 및 폴리플루오로알킬 물질(PFAS)은 환경에 광범위하게 오염되어 인간의 건강에 심각한 위험을 초래하는 고 지속성 오염 물질입니다. 효과적인 정화 전략에 대한 긴급한 요구를 해결하기 위해 흡착 기술이 PFAS 제거를 위한 유망한 접근 방식으로 주목을 받았습니다. 그러나 현재 상용화된 흡착제는 토양에서의 성능에 대한 연구가 부족하고 재생 불가능한 물질을 사용하는 등의 한계가 있다. 이러한 문제를 해결하기 위해 몬모릴로나이트 접목 키토산 비드(MTGCB)를 기반으로 하는 새로운 흡착제가 개발되었습니다. 이 논문은 물에서 PFAS 의 효율적인 제거, PFAS 로 오염된 토양에서의

안정화 및 토양의 역학적 특성에 미치는 영향을 위한 MTGCB 의 포괄적인 분석에 초점을 맞추고 이를 상용 흡착제인 입상 활성탄(GAC)과 비교합니다.

서론에서는 PFAS 가 인체 건강에 미치는 해로운 영향을 강조하여 효과적인 개선 전략의 필요성을 강조합니다. 이 연구에서 사용된 것과 같은 흡착 기술은 물에서 PFAS 를 제거하고 오염된 토양을 안정화하며 토양의 기계적 특성을 향상시키는 데 중요한 역할을 합니다. 이 연구는 세 가지 주요 구성 요소로 구성됩니다. (1) 물에서 PFAS 를 제거하기 위한 MTGCB 및 GAC 의 효율성을 평가하기 위한 흡착 테스트, (2) 토양에서 이러한 흡착제의 안정화 특성을 평가하기 위한 침출 테스트, (3) 흡착제가 토양의 기계적 성질에 미치는 영향을 조사합니다.

결과는 GAC 와 MTGCB 모두 PFAS 화합물의 효과적인 제거를 나타내며 긴 사슬 PFAS 화합물에 대해 더 높은 제거율이 관찰됨을 보여줍니다. GAC 는 모든 PFAS 화합물에 대해 24 시간 이내에 평형에 도달하는 우수한 흡착 능력을 나타내는 반면, MTGCB 는 분자 크기로 인해 24 시간인 PFBA 를 제외하고 48 시간을 나타냅니다. 두 흡착제 모두 Langmuir 및 Freundlich 모델에 잘 부합하며 MTGCB 는 소수성 및 정전기 상호 작용으로 인해 PFOS, PFBS 및 PFBA 에 대해 더 높은 용량을

나타내는 반면 PFOA 에 대해서는 GAC 와 유사했습니다. 침출 테스트는 GAC 가 최소한의 침출로 탁월한 안정화를 제공하는 반면 MTGCB 는 흡착제 비율이 증가함에 따라 침출이 감소하는 경향을 나타냅니다. PFAS 의 더 긴 탄소 사슬과 설폰 그룹은 더 나은 안정화에 기여합니다. GAC 의 경우 2%, MTGCB 의 경우 10%의 최적 첨가 비율이 토양 안정화를 위해 권장됩니다. 또한, 다짐 테스트는 낮은 비중으로 인해 두 흡착제를 추가하면 토양의 최대 건조 단위 중량이 감소하고 MTGCB 에서는 변동이 무시할 수 있는 반면 GAC 의 보수력으로 인해 수분 함량이 증가함을 나타냅니다. 그러나 마찰각과 점착력이 증가하여 GAC 의 각진 모양과 MTGCB 의 몬모릴로나이트 존재가 토양 입자를 서로 결합시키는 데 도움을 주어 기계적 특성이 개선되었음을 나타냅니다. 향상된 기계적 특성을 달성하기 위해 5%의 최적 첨가 비율이 제안됩니다. 토양의 안정화 및 역학적 특성을 고려하여 MTGCB 의 최적 첨가율은 10%로 나타났으며, GAC 의 경우 2% 첨가가 효과적인 것으로 판단된다.

전반적으로, 이 연구는 토양에서 PFAS 의 안정화를 위한 GAC 의 유망한 대안으로서 MTGCB 의 잠재력을 강조합니다. MTGCB 는 비슷한 흡착 성능, 효과적인 침출 제어 및 토양의 기계적 특성을 개선하는 능력을

보여줍니다. 연구 결과는 PFAS 제거 및 토양 안정화에 이러한 흡착제의 적용에 대한 귀중한 통찰력을 제공하여 효율적인 토양 개선 전략 및 환경 위험 평가 개발에 기여합니다.

키워드: PFAS, 교정, 흡착, 천연 흡착제, 키토산, 몬모릴로나이트, 활성탄, 침출, 안정화, 전단 파라미터.

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