Application of Modified Flax Fibres as Bio-Sorbents for the Removal of Ammonia from Liquid Phase

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Abstract

Ammonia is among the most released pollutants into Canadian waters. It is generated from a wide range of sources, including mining and agriculture, among others. The consequences resulting from high concentrations of ammonia include depletion of dissolved oxygen, lake eutrophication, and toxicity to aquatic animals. Several methods exist for the treatment of ammonia in wastewater streams, though many employ synthetic, non-sustainable materials. In turn, these create their own waste stream and can be economically unviable. As a result, interest in developing sustainable and cost-effective methods continues to be an area of research in the scope of water treatment. Biosorbents (adsorbent materials derived from organic matter) are an area of particular focus due to the sustainable and low-cost nature of these materials. Further benefits include their capacity to be modified via chemical treatments and oxidation to improve surface characteristics.

In this study, flax fibres were evaluated for their feasibility for the removal of ammonia from aqueous solution. This was achieved by conducting batch testing at various phases in the treatment and oxidation process. The goal of these tests was to establish any improvement in ammonia removal between the fibres as they were received and the fibres after undergoing treatment and oxidation. Fully treated fibres were found to have produced the largest maximum uptake capacity, based on the Langmuir model, at a value of 3.373 mg/g, a noticeable improvement when compared to the fibres as received, which achieved a maximum uptake capacity of 0.912 mg/g. The effects of varying pH and temperature on the fibres' removal capacity was also studied. The pH value that produced the most efficient removal was in the range of 6-7. The reactions occurring during removal were found to be endothermic, and indications were that the removal reaction was kinetically favorable. Additionally, thermodynamic analysis showed that favourability was increasing with increasing temperatures. Furthermore, regeneration tests were conducted for three loading and unloading cycles. A comparison of the three different regeneration solutions used indicated that 5% and 10% NaCl solutions were more effective at maintaining the fibres' uptake capacity when compared to deionized water, though results showed there was no statistical difference in the effectiveness of the 10% solution when compared to the 5% solution. In all cases, however, fibre removal capacity was declining throughout the regeneration phases.

The final phase of this study involved the characterization of the fibres' surfaces before and after treatment or testing via scanning electron microscopy (SEM), x-ray photon spectroscopy (XPS), and Fourier transform infrared

spectroscopy (FTIR) analysis. SEM imaging gave a visual analysis of the differences between fibres after various treatment stages. Results showed the removal of extractives, like lignin and hemicellulose from the fibre surface, as visual indicators of these extractives were not found in the SEM images of the treated and oxidized fibres. More detailed surface analyses using XPS and FTIR methods were helpful in confirming the removal of extractives and the presence of sodium carboxylate groups after oxidation. This further confirmed the earlier assumption that extractives had successfully been removed while also helping to determine that the oxidation procedure was a successful one.

Keywords: Ammonia, flax fibres, adsorption, TEMPO oxidation, batch testing, biosorbents, uptake capacity, surface characterization, wastewater treatment

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For Mom.

Table of Contents

List of Figures

List of Tables

List of Abbreviations

ACS: American Chemical Society

ANOVA: Analysis of variance

CNF: Cellulose nanofibrils

DO: Dissolved oxygen

FTIR: Fourier transform infrared spectroscopy

HPLC: High-performance liquid chromatography

MTZ: Mass transfer zone

MBBR: Moving bed biofilm reactor

RBC: Rotating biological contactor

RMSE: Root mean squared error

SAC: Strong acid anion

SBA: Strong base anion

SD: Standard deviation

SEM: Scanning electron microscopy

SSR: Sum of squared residuals

STP: Standard temperature and pressure

TAN: Total ammonia nitrogen

VOC: Volatile organic compound

WAC: Weak acid cation

WBA: Weak base anion

XPS: X-ray photoelectron spectroscopy

List of Nomenclature

A^+: Ion A

B^+: Ion B

b: Langmuir Isotherm Constant

C^0: Degrees Celsius

C_o, C_i: Initial aqueous phase contaminant concentration

C_{eq}: Equilibrium phase concentration

cm: Centimeter

cm^{-1}: Reciprocal centimeter

eV: Electronvolt

ΔG: Gibbs free energy

g: Grams

ΔH: Enthalpy change

h: Hours

K_a: Acid ionization constant

K_A^B: Selectivity of ion B over ion A for a particular resin

K_F: Freundlich Isotherm Constant

K_L: Langmuir constant at a given temperature

k, k_2: Rate constants of the pseudo-first order and pseudo-second order models, respectively

kV: Kilovolts

L: Litres

LC_{50}: Unionized ammonia concentration that produces a 50% mortality rate

M: Mass

mg: Milligrams

min: Minutes

mL: Millilitres

mm: Millimetres

1/n: Freundlich Isotherm Exponent

n: Valence charge of respective ion

nm: Nanometers

pK_a: Acid dissociation constant

Q_{max}: Maximum adsorption capacity

q_e, q_{eq}: Equilibrium solid phase contaminant concentration

q_i: Initial solid phase contaminant concentration

q_t: Uptake capacity at time t

R: Universal gas constant

R^2: Coefficient of determination (R squared value)

rpm: Rotations per minute

ΔS: Entropy change

T: Temperature

t: Time

V: Volume

w: Adsorbent dose

Chapter 1: Introduction

1.1 General Background

Ammonia has been identified as the second most released pollutant by mass into Canadian water systems, second only to the nitrate ion (Environment and Climate Change Canada, 2017). Various sources, including municipal wastewater, the mining industry, the manufacturing industry, and the agricultural sector, all contribute to ammonia discharge into the environment. Several concerns can arise associated with high concentrations of ammonia in aquatic environments. This creates a need for its removal before releasing effluent into receiving water bodies. At high concentrations, ammonia can be toxic to aquatic organisms (Soler et *al.,* 2021). Furthermore, nitrogen found in ammonia acts as a nutrient that promotes the growth of plants and algae; excessive growth can lead to eutrophication and further limit the dissolved oxygen available to aquatic species due to nitrification, an oxygen-consuming process (Environment and Climate Change Canada, 2021; Environment Canada, 2001).

Methods of treatment for ammonia are often biological in nature, implementing the nitrification/denitrification process in which ammonia is converted to nitrogen gas via bacteria. Other methods include air stripping, in which the volatile nature of ammonia in its unionized form is taken advantage of for removal via volatilization (Ronan et *al.,* 2021; Srinivasan et *al.,* 2009). Furthermore, ion exchange is a method in which media containing charged ions can exchange those ions with ammonia in solution (Ding & Sartaj, 2015). These techniques, however, each come with drawbacks, including the production of sludge or difficulties managing changes in the influent wastewater characteristics. There are also concerns relating to operation costs and the sustainability of these methods (Bello et *al.,* 2016; Chartrand, 2018).

Particularly with ion exchange, there is interest in developing more sustainable and cost-effective materials for the removal of ammonia as well as other contaminants. Many materials currently implemented in contaminant removal are of synthetic or non-renewable origin, leading to the production of further waste products as these materials reach their service life. Biosorbents, referring to ion exchange materials derived from organic wastes such as plant matter, are being researched as an alternative material to these non-renewable sources like zeolites and synthetic resins (Bello et *al.,* 2016). Studies have shown that biosorbents derived from algae, food waste, and agricultural waste can remove a variety of pollutants, including, but not limited to, heavy metals, dyes, and ammonia (Osman et *al.,* 2023). Cellulose-based materials are of special interest in the development of biosorbents. Their properties, particularly the surface

function groups and capacity for chemical modifications, in addition to benefits in cost and sustainability, make them a good candidate as a treatment material. Specifically, a cellulosic material's versatile surface chemistry contains many functional groups, some of which can be altered to carry ions that can be exchanged with ammonia for removal. This property creates a strong potential for modification; in particular, the hydroxyl groups on the surface are an ideal candidate for functionalization using the TEMPO radical, a chemical compound used as a catalyst for the oxidation of primary alcohols. TEMPO oxidation has been studied with various materials and is a proven method for efficient, selective oxidation of cellulose (Tang et *al.,* 2021; Ong et *al.,* 2022). Being a selective oxidizer means the process only alters targeted sites on the cellulose surface, and in the case of the TEMPO radical, it is these hydroxyl groups that are selected and functionalized to carboxyl groups bonded with a Na^+ ion. One additional benefit of this high selectivity is increased preservation of the cellulose structure when compared to other oxidation methods. In addition, TEMPO oxidation is performed in mild conditions compared to other methods, further preserving the structure of the material while limiting side reactions and ensuring the proper functional groups are altered at high efficiency (Saito et *al.,* 2007).

Canada is one of the top producers of flax seeds in the world; however, the resulting waste products are typically discarded or burned instead of seeking a functional application, as insulation or in composite materials, for example (Foruzanmehr et *al.,* 2014; Reany et *al.,* 2006). Flax fibres, with a make-up of roughly 70% cellulose and being in abundance, form an ideal candidate for a sustainable biosorbent material. Several studies have been conducted on the oxidation of flax fibres. These cover topics including their use in composite materials and as a treatment medium, though limited work has been done in relation to the removal of nitrates (Foruzanmehr et *al.,* 2014; Abbar et *al.,* 2017). Given the desire to develop low-cost, effective, and sustainable methods that are also easily implemented, TEMPO oxidized flax fibres will be investigated as a viable option for the removal of ammonia from aqueous phase.

1.2 Objectives

The main objective of this study is to assess and optimize the performance of chemically treated flax fibres for the removal of ammonia from aqueous phase. This was achieved by iterations in the treatment and oxidation methods and the comparison of the results of batch adsorption tests at various stages along the process. More specifically, the goals of this study are as follows:

- Assess the effectiveness of the TEMPO oxidation method and the extent of the functionalization achieved after fibres have undergone chemical treatments and TEMPO oxidation.
- Assess the performance of fibres using batch adsorption experiments and determine any levels of improvement in removal capacities before, during, and after all chemical treatments and TEMPO oxidation.
- Assess the performance of functionalized fibres under various conditions, including changes in initial concentration, temperature, and pH.

1.3 Thesis Layout

The thesis is divided into five chapters. Beginning with an introduction in chapter one, this covers a brief outline of the issues with ammonia and removal methods, as well as the objectives of the research and the layout of the thesis. Chapter two is a literature review that goes into more detail on ammonia, the various removal methods currently in use, and biosorbents as an emerging media, along with the TEMPO-mediated oxidation process and the use of flax fibres. This chapter will also briefly discuss the research gap addressed in this thesis. Chapter three goes over the materials used and describes the experimental and analytical methods applied. The fourth chapter is a technical paper titled "Ammonia Removal from Aqueous Solution Using Novel Biosorbent Developed from TEMPO Oxidized Flax Fibres." Covered in the paper are the results of batch adsorption experiments using fibres at various stages of the treatment and oxidation processes. This serves to create a better understanding of any differences in the effectiveness of the fibres based on the level of treatment and looks at the potential mechanisms of removal. Furthermore, it covers the results of testing conducted under differing conditions to establish the impact this has on the fibres adsorption capacity. Finally, the last chapter contains conclusions gathered during the study and presents suggestions for other similar works that may be undertaken in the future.

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Chapter 2: Literature Review

This chapter presents an overview of fundamental details about ammonia and how its presence can affect aquatic ecosystems. It also encompasses a variety of strategies that are used for the treatment of ammonia, including materials and treatment methods, with an emphasis on the ion exchange processes. Additionally, it includes a discussion of biosorbents and their application in adsorption and treatment processes, along with a look at the treatment and modification methods that are being studied in relation to improving the removal efficiency of these biosorbents.

2.1 Ammonia

Ammonia is a colourless, pungent-smelling compound composed of hydrogen and nitrogen, whose distinct tetrahedral structure influences its properties and behaviours. Ammonia, particularly ammonium nitrate (NH_4NO_3), can be widely applied to industrial processes, from fertilizers to explosives. Furthermore, ammonium hydroxide's (NH_4OH) ability to readily dissolve in water enables its use in a wide range of cleaning products (New York State Department of Health, 2005; Environment Canada, 2001). Depending on temperature and pH conditions, ammonia can exist in two distinct forms: unionized ammonia NH_3, and its ionized form, referred to as ammonium ion or ionized ammonia, NH_4^+. The following equations indicate the link between these two compounds.

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \quad \text{(eq. 2.1)}$$

$$K_a = \frac{[NH_3] \cdot [H^+]}{[NH_4^+]} = 10^{-pK_a} \quad \text{(eq. 2.2)}$$

Where $[NH_3]$, $[NH_4^+]$, and $[H^+]$ are molar concentrations of ammonia, ammonium, and hydrogen ions, respectively. K_a and pK_a represent the equilibrium constant, a function of temperature. The value of pKa for ammonia at 25 ºC is 9.24 (Halling-Sørensen and Jorgensen, 1993). Due to the potential fluctuations of these two species in solution, total ammonia nitrogen (TAN) is commonly used to show the combined concentration of ammonia and ammonium ions. At 25 ºC and standard temperature and pressure (STP), Figure 2.1 can be used to find the concentration of each species with respect to pH. The concentration of NH_4^+ is almost 100% at pH values below 7, decreasing to 50% at 9.24, and finally reaching 0% at pH levels above 12. Both forms of ammonia will have impacts on the aquatic environment if they are released in excessive amounts. The unionized form (NH_3) can be particularly

harmful, however, as it is acutely toxic to all aquatic life. Prolonged exposure to this form has also been found to have harmful effects on humans (Soler et *al.,* 2021).

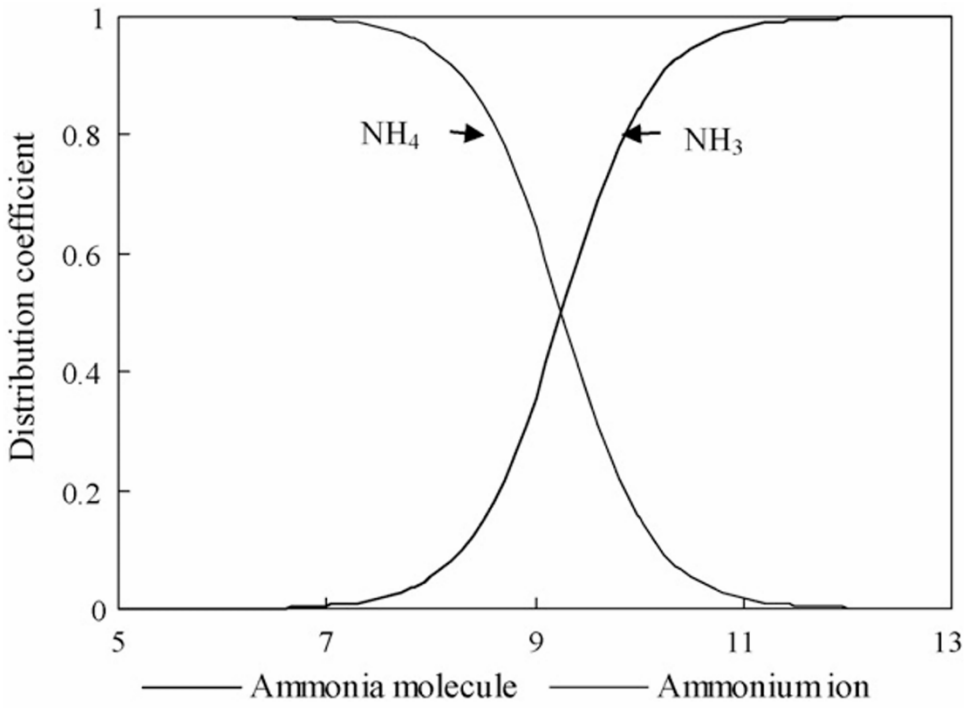

Fig. 2.1: Distribution of NH_3 and NH_4 at different pH values (Lin et *al.,* 2009)

2.1.1 Ammonia in the Environment

Several sources of TAN discharge into the aquatic environment exist, primarily from agriculture (especially fertilizers and animal-rearing), municipal and mining wastewaters, and other industries such as food processing and pharmaceutical production. TAN from these sources can enter in a direct manner, via effluent discharge and mining or agricultural runoff, or indirectly via groundwater contamination (Environment Canada, 2001; Environment Canada, 2010). In 2019, an estimated 69,000 tons of ammonia were released in Canada, of which 50,400 tons were released into aquatic sources. Between 2015 and 2019, this value saw a roughly 15% increase (NPRI, 2024).

When released at elevated levels, excess TAN will have various negative effects on the aquatic environment. These include depletion of dissolved oxygen (DO), eutrophication, and toxicity to aquatic life. Firstly, DO depletion can occur under conditions of excess TAN due to nitrification. This occurs when aerobic bacteria convert ammonia to nitrate in a process that demands large amounts of oxygen to complete. The resulting nitrification will lead to the consumption of oxygen at a rate that can limit the amount of DO. Available oxygen could inevitably drop to levels

that some aquatic life cannot sustain, as they rely on DO for respiration (Constable et *al.,* 2003). Nitrogen is also a major nutrient, or fertilizer, which can accelerate plant and algae growth. The nitrogen from TAN can be used by plants and algae to promote growth and can reach a point where excess growth promoted by excess TAN will create surface buildup, or algal blooms, thus impeding sunlight from penetrating through the water source. In turn, this prevents plants at the bottom of the aquatic environment from photosynthesizing, further reducing DO levels. In addition, when accumulated biomass dies off in large numbers, it creates more demand for DO through biological aerobic decomposition (Water Resources Mission Area, 2019). Moreover, a direct impact of TAN at exacerbated levels is toxicity to fish and other aquatic species. Unionized ammonia is acutely toxic and leads to symptoms such as gill damage, respiratory problems, changes in swimming and feeding behaviours, and eventually death with prolonged, high-level exposure. Furthermore, this toxicity can extend to prolonged or high concentration exposure in humans, where symptoms can include skin and respiratory irritation as well as digestive tract issues (Soler et *al.,* 2021).

As a result of these factors, limits on TAN discharge have been set to protect environments that are at risk of exposure. Ammonia is defined as a toxic substance by the 1999 Canadian Environmental Protection Act, which allows for its regulation. Impact on aquatic life is a deciding factor in determining discharge limits, and research done by the Canadian Government provides an important benchmark using LC_{50} values, or the unionized ammonia concentration that produces a 50% mortality rate, for various native fish species. In Canada, LC_{50} values can range from 0.279 mg NH_3/L up to 1.860 mg NH_3/L based on the species in question and other existing conditions in the aquatic environment. As a conservative estimate based on previous studies, Environment Canada has set the recommended limit for freshwater bodies at 0.019 mg NH_3/L. On effluent concentrations, the Fisheries Act has established a maximum discharge of 1.25 mg NH_3/L at 15 ºC ± 1 ºC (Environment Canada, 2001; Environment Canada, 2010; ECCC, 2017).

2.2 Treatment of Ammonia in Wastewater

2.2.1 Air Stripping

Air stripping is a process that takes advantage of the volatile nature of TAN to facilitate its removal by diffusing it from wastewater into the air. It is a method that has seen a wide range of applications for the removal of volatile organic compounds (VOCs). The idea behind any air stripping treatment apparatus is to establish maximum contact between the wastewater stream and air to increase the efficiency of TAN removal through volatilization, and this is seen in the common types of air stripping setups such as packed towers and diffuse aerators (Srinivasan et *al.,*

2009). A packed tower consists of a large, cylindrical column that is filled with packing material, typically an inert solid such as plastic, and inlets at the top and bottom of the column for wastewater and gas, respectively. Wastewater enters the inlet and begins to trickle down the system while air is simultaneously blown up through the system. The packing material will distribute the inflowing water, creating random flow paths and thus increasing the surface area for more volatilization of the TAN as air flows up through the system (Zangeneh et *al.,* 2021). Other examples, such as tray stripping, employ a similar principle but may alter the packing material or direction of flow for the air and wastewater (WTFSAS*,* 2000).

The volatility of a substance, describing something's ability to readily evaporate into the air, plays a significant role in the efficiency of the air stripping method. In the unionized form, ammonia is more volatile; it is therefore common to increase the pH of the incoming wastewater to 10.8-11.5 for an increased concentration of unionized ammonia and increased removal efficiency. In practice, efficiency has been shown to reach upwards of 90% ammonia removal at temperatures of 20 ºC and above (WTFSAS, 2000). However, there are some disadvantages that impact the effectiveness of this method. Air stripping suffers greatly in low-temperature environments, with efficiency reducing to 75% or lower at 10 ºC and a risk of wastewater freezing in the system. These factors would limit the feasibility of this method, especially in the northern communities of Canada, where icing and low efficiency would be exacerbated (Zhang et *al.,* 2022). If heating is required, then the system will require more energy, resulting in increased operating costs. Adequate aeration in the system can also be impacted by surfactants and the buildup of contaminants in the system (Kar et *al.,* 2023; Zangeneh et *al.,* 2021).

2.2.2 Biological Treatment

Biological treatment is one of the more common methods for the removal of TAN, especially at low concentrations, such as municipal wastewater. This process takes advantage of certain organisms' metabolic activity to convert TAN into other nitrogen compounds that are less harmful. More specifically, a biological process called nitrification occurs in which ammonia is oxidized to nitrite (NO_2^-) and then to nitrate (NO_3^-). A complementary process called denitrification will then occur, converting the new nitrate compounds into nitrous oxide (N_2O) and nitrogen gas (N_2), thus completing the nitrogen cycle (Liu et *al.,* 2023; Ronan et *al.,* 2021). The following figure denotes the nitrification/denitrification process.

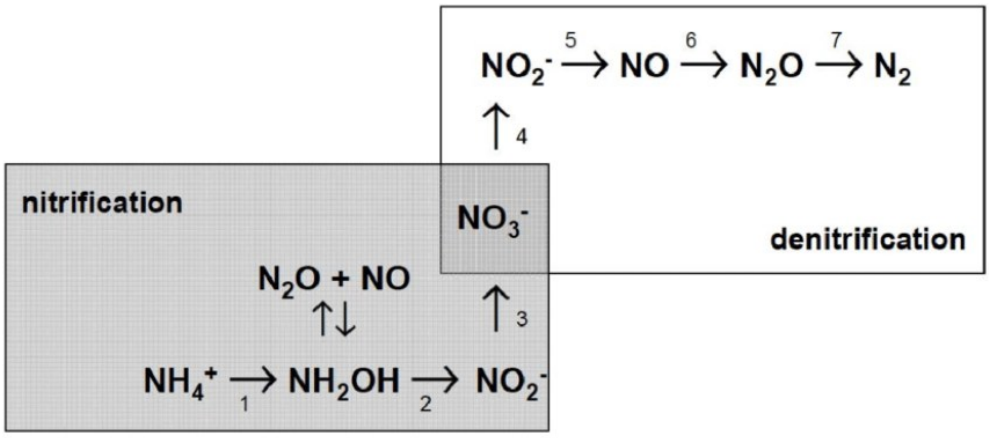

Fig. 2.2: Nitrification/denitrification process (Migliorati, 2015)

Two main types of biological systems are commonly used in TAN treatment: suspended growth systems and attached growth systems. One of the most prevalent biological systems is the activated sludge process, a suspended growth system. This system uses flocs, essentially aggregated bacterial cultures, which are suspended in wastewater via aeration that also supplies the oxygen necessary to allow the bacteria to complete the nitrification process. Upon reaching a large enough size, these flocs will settle, accumulate, and be effectively removed from the system as what is called sludge. The sludge itself removes a portion of the ammonia nitrogen due to the new biomass produced (Varhelyi et *al.,* 2019). Widely implemented for municipal wastewater treatment, activated sludge systems are known for their highly effective TAN removal capabilities and adaptability to manage various influent loads and characteristics. Examples of limitations in this system include the sludge produced, which requires separate treatment and disposal, and the risk of shock to the system, be it a sudden toxic load or an increase in organics, which can disrupt the bacteria present in the system and impact efficiency (Hauduc et *al.,* 2012).

For attached growth systems, one of the more common examples is the moving bed biofilm reactor (MBBR). This technology operates on a similar basis to activated sludge, with the main difference being that bacteria are attached to a medium, typically a plastic carrier, which is suspended in the wastewater via aeration or mechanical agitation. Advantages of this system include a more stable environment for bacteria growth, a more compact footprint, and generally less energy consumption than activated sludge systems (Liu et *al.,* 2023). Other examples of attached growth systems are rotating biological contactors (RBC) and trickling filter systems. A different approach is used where nitrifying bacteria is attached to a larger medium and wastewater is brought into contact with the cultures for

the treatment to occur. This is done through a series of natural or synthetic media beds in the case of trickling filters or by rotating discs with attached bacteria through wastewater tanks in the case of RBC (Henderson & Atwater, 1995).

2.2.3 Other Methods

Various other methods exist for the removal of TAN. Breakpoint chlorination is an oxidation method in which chlorine added to a solution will react with TAN, converting it to chloramines and eventually into the final byproducts of nitrogen gas and water. One issue with this method, however, is that it becomes impractical for high TAN concentrations due to the extremely high chlorine doses required (Paul et *al.,* 2017). Membrane filtration is another example, utilizing reverse osmosis and nanofiltration to capture TAN molecules as a solution is passed through a semi-permeable membrane (Rohani et *al.,* 2021). Microwave radiation and chemical precipitation are examples of other methods; however, they are typically quite resource-intensive and not as effective as the previously discussed methods for TAN treatment (Dong & Sartaj, 2015).

2.2.4 Ion Exchange

2.2.4.1 Introduction

Ion exchange can be defined as a process by which ions in a liquid solution are exchanged with ions on, and subsequently bind to, the surface of a solid material, referred to as the ion exchange medium. These materials, sometimes called adsorbents, can be natural or synthetic, are often highly porous, and contain ions on the material's pore walls that facilitate ion exchange. This process is applicable to various areas, including water treatment and industrial processes. It is even the method applied to most at-home water purification filters (Jorgensen & Weatherley, 2003). In early applications, natural materials like clay and mineral soils were the predominant adsorbents. Further understanding of the properties of these early media would eventually lead to the discovery of natural minerals called zeolites, which in turn gave rise to the development of synthetic mediums often seen in modern ion exchange apparatuses (Farooq et *al.,* 2020).

2.2.4.2 Ion Exchange Materials

2.2.4.2.1 Zeolites

Derived from crushed aluminosilicate minerals, natural zeolites are a common ion exchange material known for their high porosity and ability to selectively capture and remove contaminants from solution. Zeolites are mined

and produced globally, with chabazite and clinoptilolite being the most common forms (Lima et *al.,* 2019). Their porous, cage-like structure is produced from the tetrahedral linkage of aluminum and silicon bonded to oxygen, which form a consistently arranged three-dimensional structure, shown in figure 2.3.

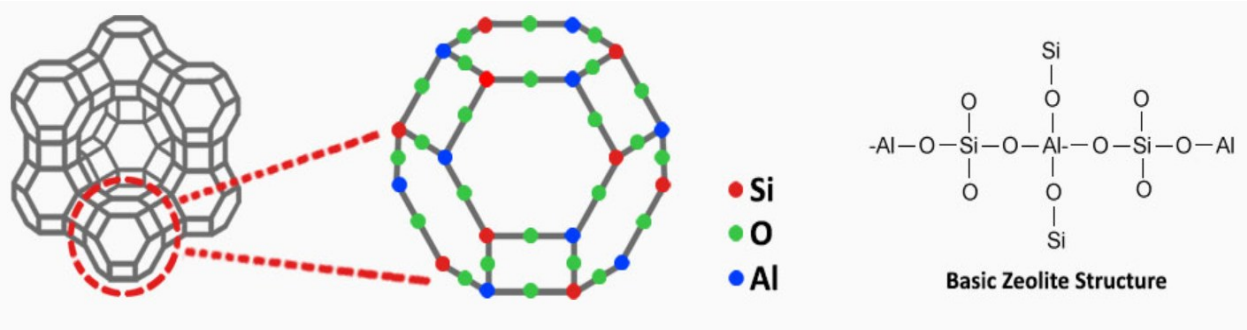

Fig. 2.3: Basic structure of natural zeolites. (What is zeolite?, n.d.)

Atomic makeup, structure, and pore size will vary between different minerals and create variations between distinct types of zeolites; however, the same general atomic formula can still be applied to all types (Huang et *al.,* 2015).

$$\left(M_x^+, M_y^{2+}\right)\left(Al_{(x+2y)}Si_{n-(x+2y)}\right)\cdot mH_2O$$

Where M^+ and M^{2+} represent the cations, known as the exchangeable ions (Na^+, K^+, and Ca^{2+}). Regardless of their exact composition and structure, all zeolites facilitate ion exchange through their nanoporous structure and high surface area. Ion exchange is driven by the exchangeable ions already present in the zeolite structure (Margeta et *al.,* 2013). The aluminum sites, resulting from the substitution of silicone by aluminum, are negatively charged and therefore constitute the site of ion exchange, with positively charged cations being bound to these sites. The ion exchange capacity of a zeolite is therefore directly related to the ratio of aluminum to silicone found in the structure. From this, it can be inferred that a zeolite with a higher alumina content will be more effective at capturing high-charge cations. Conversely, a zeolite with a high concentration of silicate would preferentially attract molecules with less polarity (Akerele et *al.,* 2023; Margeta et *al.,* 2013).

Synthetic zeolites, developed from natural zeolites, are a more recent advancement in ion-exchange materials. Compared to natural zeolites, the greatest difference is the control over the properties of the material. Properties can

be tailored during the manufacturing process to improve metrics like pore size, surface area, ion count, and ion selectivity. Typically, this allows for overall improvements in the characteristics of synthetic zeolites over natural ones (Król, 2020). Synthetic zeolites are produced by combining specified ratios of silica, alumina, and other chemicals in water under elevated temperature and pressure—a process called hydrothermal synthesis. In particular, the Si:Al ratio will determine the ion exchange properties of a synthetic zeolite. In the case of TAN removal, synthetic zeolites that are hydrophilic with a low Si:Al ratio are ideal (Sommerville et *al.,* 2013).

2.2.4.2.2 Synthetic Resins

Synthetic resins (figure 2.4) originated in the mid-1940s, as work was being done to develop an ion exchanger with greater stability and efficiency than zeolites provided at the time. Resins will undergo chemical treatment that binds functional groups within the material, and it is the functional groups present that determine the classification of said resin (Water Handbook, n.d.). The four most common classifications are:

- Weak Acid Cation (WAC) and Strong Acid Cation (SAC)
- Weak Base Anion (WBA) and Strong Base Anion (SBA)

Acid cation ion exchange resins hold negatively charged ions fixed to their functional groups and will be selective towards exchanging with positively charged counter-ions in solution. The opposite is true for the base anion exchangers. In the case of TAN, the proper resin to use for its treatment would be acid cation exchangers, due to the positive charge of the ammonia ion (Marshall, 2017). Several studies have been conducted and have shown that several types of acid cation exchangers are effective at the treatment of ammonia in a range of wastewater sources (Zhang et *al.,* 2022; Farooq et *al.,* 2020; Ding & Sartaj, 2016; Sica et *al.,* 2013). A significant advantage of resins over other ion exchange materials is their ability to customize their characteristics during production. Tailored structure and functionalized groups allow for resins to be designed with affinity for a specific contaminant in mind. This can be particularly important when dealing with wastewater containing several pollutants. Additionally, resins are typically known to have greater stability and adaptability, in that they are better equipped to handle changes in pH, concentration, and temperature. Regeneration of resins will depend on the classification and on what ion is being removed from solution; salt, acid, and caustic solutions are often used as regenerants (Alexandratos, 2008; Marshall, 2017).

Fig. 2.4: Ion-exchange resin beads. (Ion Exchange in water treatment, 2022)

2.2.4.3 Selectivity

When selecting an ion exchange material, a key factor to consider is the selectivity of said material. Selectivity can be described as a material's order of preference or affinity towards certain ions over others in solution (Crittenden, 2012). The selectivity of an ion exchanger will be determined by the physical and chemical properties of both the exchange material and the counter-ion(s) present in solution. More specifically, the pore size of the material and the function groups found on its surface control its selectivity. Similarly, the ionic charge and radius of the contaminant(s) found in solution will play a roll in determining which are preferentially exchanged (Edzwald, 2011). In a binary system, the selectivity of a resin can be calculated by finding the selectivity coefficient, K_A^B, using the following equation:

$$K_A^B = \frac{(A^+)^n (RB^{n+})}{(RA)^n (B^{n+})} \qquad \text{(eq. 2.3)}$$

Where A and B are concentrations of ions A and B in solution, RA and RB are the solid-phase equivalent concentrations of ions A and B (mass of ion adsorbed per mass of ion exchange material), and n is the valence charge of the respective ion. The higher the selectivity coefficient, the higher the affinity of a particular resin will be for that ion (Edzwald, 2011).

The order of affinity will vary between zeolites and depends on the size of pores, the charge of cations present in the material, and the number of exchange sites, among other factors. It is therefore necessary to perform various tests in order to determine the selectivity of a particular zeolite. Clinoptilolite is an example of zeolite that is known for its good affinity for ammonia and has a well-documented order of selectivity, as follows (Rahmani et *al.,* 2004):

$$K^+ > NH_4^+ > Na^+ > Ca^+ > Mg^{2+}$$

2.2.4.4 Process Operation

The ion exchange process is typically operated under one of two systems, either batch or continuous flow. The first option, batch operation, is a simple and flexible treatment method that involves brining ion exchange media in contact with solution in a closed system. The media and solution are kept in this closed environment, normally with some level of shaking or mixing, for sufficient time to allow ion exchange to occur. The simple nature of this method makes it an ideal candidate for small-scale operations and research rather than large-scale treatment applications (Pourhakkak et *al.,* 2021; Davis, 2020).

More often used at the industrial scale are continuous flow systems; cylindrical vessels referred to as ion exchange columns are large containers packed with ion exchange media used in this process. The basis of this method is to flow a solution through the column, allowing it to contact the ion exchange materials and remove the unwanted contaminant. As the solution flows through the column, the materials will eventually become saturated with ions until the column needs regeneration (Davis, 2020; Wachinski, 2016). Figure 2.5 provides a diagram of this process at various stages along the cycle.

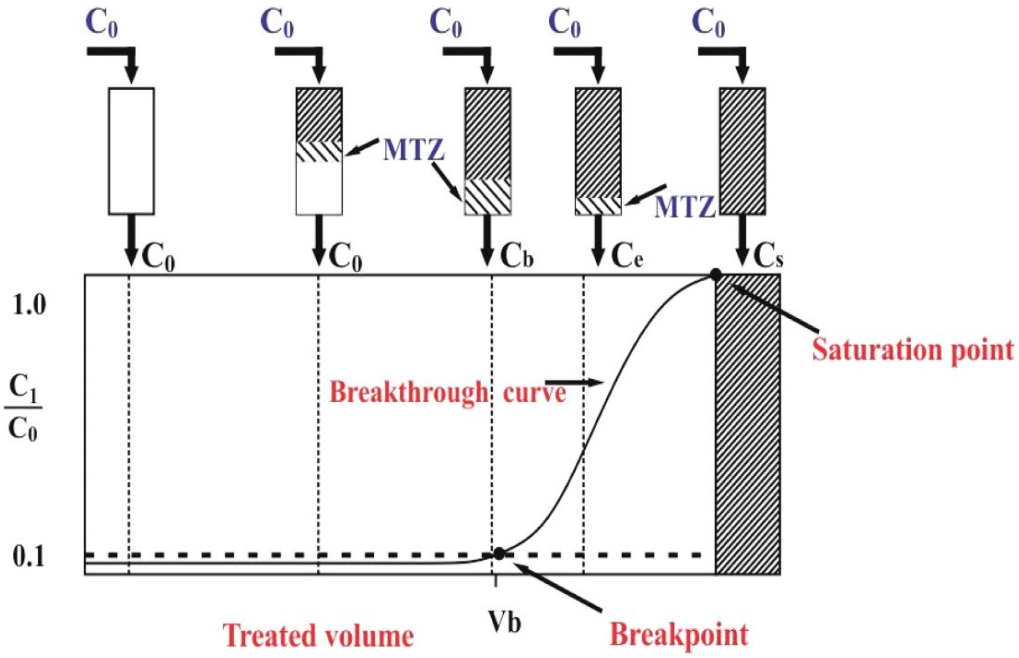

Fig. 2.5: Fracture curve and mass transfer zone movement of an ion exchange column. (Pourhakkak et *al.,* 2021)

Initially, the column is packed with unsaturated ion exchange media and will remove all traces of the target ion as the solution passes through. The column will begin to saturate as time progresses, forming a mass transfer zone (MTZ), sometimes called the exchange zone (EZ), which will eventually reach the end of the column (Pourhakkak et *al.,* 2021). Once the MTZ has reached the end, an event referred to as the breakpoint, the column becomes sufficiently saturated that not all target ions will be removed, and the effluent concentration contains some of these ions. If left to continue running, the effluent concentration will eventually match the influent concentration; this is why, when the saturation point is reached, the column is taken offline for regeneration. For this reason, it is typical to see systems using ion exchange columns use more than one, so that as one column is being regenerated, the other(s) can be used for treatment (Gabelman, 2017).

2.2.4.5 Regeneration

Regeneration is the process by which an ion exchange material can be restored once it has reached saturation during treatment. Typically, it involves the use of a regenerant solution, which acts to remove the contaminant ions collected on the material and replace them with fresh counterions to renew its exchange capacity (Hedstrom, 2001). Some of the most common regenerants are highly concentrated sodium solutions, which take advantage of high

concentrations to overcome selectivity. As discussed previously, most ion exchange materials show an order of preference in what ions are exchanged; however, highly concentrated solutions (often 100 times greater than the concentration of the contaminant ion) will cause the selectivity order of the material to reverse (SenGupta, 2017; Crittenden et *al.,* 2012). Sodium regenerant solutions are preferred for their compatibility and versatility. They are relatively inert and compatible with many zeolites and synthetic resins, which minimizes the degradation of materials. Other examples of regenerants include acidic solutions, such as hydrochloric acid, which are commonly seen in systems using SAC/WAC exchange materials (Zhang, 2022). Conversely, basic solutions, like those prepared with sodium hydroxide, are often used in the regeneration of SBA/WBA ion exchange materials (Li et *al.,* 2016). The process by which a material is regenerated is similar to how the system is run during the treatment process. After backwashing the column or bed to remove any debris collected during treatment, a regeneration solution is allowed to flow through the material. This step displaces any captured ions before a final rinse is done to clear any residual regenerant solution (SenGupta, 2017). The main concern associated with the regeneration process is the management of used regenerants. These can be an environmental hazard due to contaminants now being present in the solution. In the case of TAN removal, NH_4^+ now concentrated in solution must be removed before disposal or reuse of the regenerant, which creates the need for further treatment (Maul et *al.,* 2014; Crittenden et *al.,* 2012). As a result, these environmental concerns generated interest in researching alternate methods for regeneration such as chlorine regeneration (Narbaitz et *al.,* 2023).

2.2.4.6 Modeling of Batch Testing

Modeling is done to find or predict the behaviour of an ion exchange process based on the results of small-scale batch testing. The most common method is to perform equilibrium tests of various contaminant concentrations and relate them to a model known as an isotherm model, which derives its name from the fact that tests are performed at a constant temperature (Amrutha et *al.,* 2023; Kalam et *al.,* 2021). The goal is to establish a relationship between the equilibrium solid phase concentration (q_{eq}, mg/g), a measure of the mass of contaminant adsorbed on unit mass of ion exchange media, and the equilibrium liquid phase concentration (C_{eq}, mg/L), the final concentration of contaminant in the solution at equilibrium (Ayawei et *al.,* 2017). The following equation outlines this mass balance:

$$V \cdot C_i + M \cdot q_i = V \cdot C_{eq} + M \cdot q_{eq} \qquad \text{(eq. 2.4)}$$

Where V is the volume of solution (L), C_i is the initial aqueous phase concentration of contaminant (mg/L), M is the mass of contaminant (mg), and q_i and q_{eq} are the initial solid phase and equilibrium solid phase concentrations, respectively (mg/g). Several modeling techniques exist for the interpretation of this data, each with distinctive characteristics that make them more applicable to certain conditions or systems. Two of the more basic models include the Langmuir isotherm and Freundlich isotherm models (Ayawei et *al.,* 2017).

2.2.4.6.1 Langmuir

The Langmuir isotherm is a widely used and simple model that aims to produce important adsorption parameters. Namely Q_{max}, the maximum capacity for substance exchange per unit mass of media, and b, the Langmuir constant related to the strength of interaction between ions and exchange media. Proposed in 1916 by Irving Langmuir, the model applies several assumptions: Adsorption occurs in a single layer (monolayer) on the media surface; there are a finite number of identical sites available for exchange or adsorption; and there will be no interaction between ions once they occupy a site (Nix, 2015; Ayawei, 2017; Swenson & Stadie, 2019). The model applies the following equation to find equilibrium solid phase concentration:

$$q_{eq} = \frac{b \cdot Q_{max} \cdot Ceq}{1 + b \cdot C_{eq}} \qquad \text{(eq. 2.5)}$$

Where q_{eq} is the equilibrium solid phase concentration (mg contaminant/g media), b is the Langmuir constant (L/mg), Q_{max} is the maximum adsorption/exchange capacity (mg/g), and C_{eq} is the equilibrium phase concentration (mg/L).

2.2.4.6.2 Freundlich

The Freundlich isotherm is another broadly used model and is one with a slightly more flexible interpretation of the mechanisms of ion exchange. Major differences compared to the Langmuir model include the assumptions that the surface is non-uniform with various adsorption mechanisms and that there is the possibility of multilayer adsorption and exchange. This model seeks to determine two parameters: the Freundlich constant, a measure of the capacity of the surface, and the Freundlich exponent, a measure of adsorption or exchange intensity (Kalam et *al.,* 2021; Ayawei, 2017; Van Der Bruggen, 2014). The model applies the following equation to find equilibrium solid phase concentration:

$$q_{eq} = K_F \cdot C_{eq}^{\frac{1}{n}} \quad \text{(eq. 2.6)}$$

Where q_{eq} is the equilibrium solid phase concentration (mg contaminant/g media), K_F is the Freundlich adsorption constant (L/mg), C_{eq} is the equilibrium phase concentration (mg/L), and *1/n* is the Freundlich exponent.

2.3 Biosorbents for the Treatment of Ammonia

2.3.1 Biosorbents

The search for low-cost, abundant, and sustainable materials with effective treatment properties has been a focus in the wastewater treatment field in recent years. The application of biological materials, such as plants, microorganisms, and agricultural waste, as shown in Figure 2.6, has gained widespread attention as they typically meet these criteria. Biosorbents can be defined as any biological material used for the removal of a pollutant from a solution (Wang & Chen, 2009; Vijayaraghavan & Yun, 2008). Various important functional groups exist in these materials that provide the driving force for the treatment of pollutants, like what is seen with zeolites and resins. Various biosorbents have been studied to show their sorption capacities; however, a large variety in capacity, selectivity, and regeneration potential can create a challenge in showing the most effective biosorbent for a pollutant from a wide selection of abundant and low-cost materials (Dey et *al.,* 2021). An additional useful property of biosorbents is their ability to be modified via treatment. These materials allow for easy removal of impurities and improvements in uptake capacity. Considering the nature of most biosorbents, particularly plant-based materials, there is the potential for the leaching of organic matter like lignin and hemicellulose into solution. Treatments can be used, such as chemical or thermal, to remove these substances (Wang & Chen, 2009). A further benefit of these treatments is their ability to modify or increase the exposure of the functional groups found in the material. Further exposure of functional groups also provides the capacity to modify the material via oxidation, a topic that will be expanded on in a later section (Fathi et *al.,* 2019).

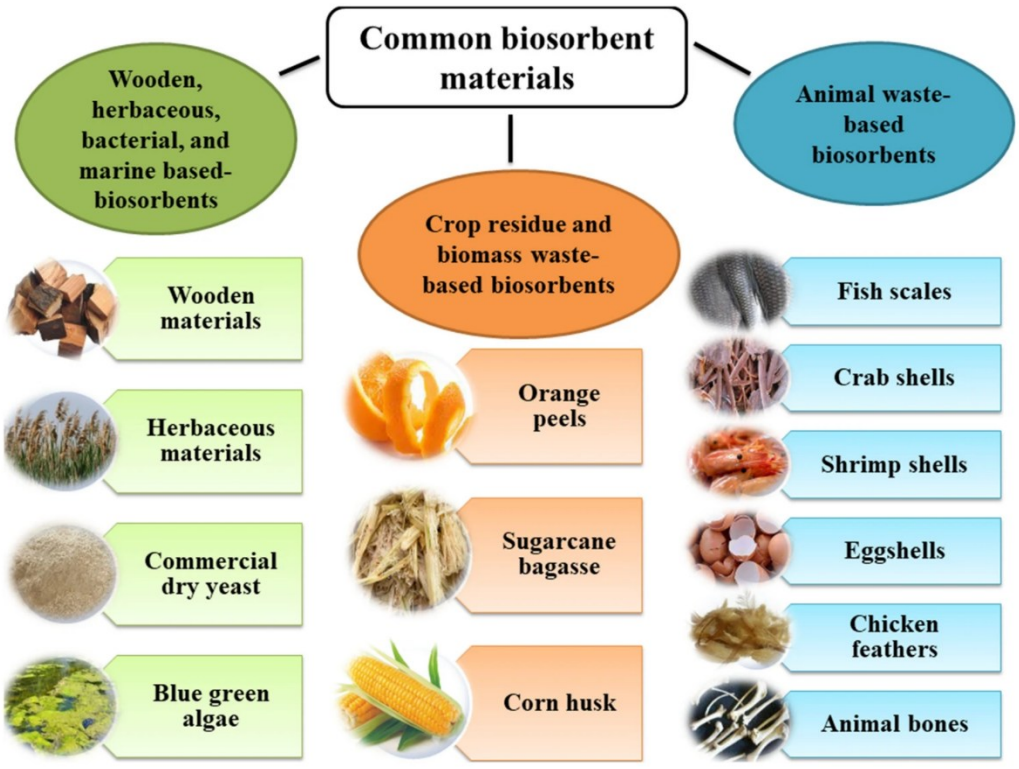

Fig. 2.6: Categorization of commonly used biosorbents (Osman et *al.,* 2023)

Work with biosorbents has shown successful removal of a range of pollutants, including heavy metals, dyes, and pharmaceutical waste, implementing various biosorbents from bacteria to agricultural waste. Black et al. (2014) detailed the potential for immobilized microorganisms to adsorb copper and lead from solution by attaching them to polystyrene carriers. It was concluded that removal rates for fixed bacteria reached 97.5% and 83.7% for copper and lead, respectively. Similarly, a study by Kumar and Sahu (2013) showed that waste generated from sugar cane production (bagasse) was also successful in the treatment of heavy metals, able to reach over 90% removal of cadmium and iron ions. Studies on the application of biosorbents for the removal of TAN, such as those by Reddy et al. (2015), which detailed the use of banana peel to treat nitrates, are also being conducted. Dried and powdered peels achieved nearly 80% removal of TAN in solutions with concentrations up to 200 mg/L. Khalil et al. (2018) detailed comparable results applying rice straw waste for TAN treatments. In this case, sodium hydroxide treatment followed by high temperature thermal activation was applied to enhance the effectiveness of the rice straw and recorded removal efficiencies of 50-70% with the maximum adsorption capacity reaching 4.5 mg/g.

2.3.1.1 Cellulose

Cellulose, a biopolymer found in plants, animals, and bacteria, has been of particular interest in the development of biosorbents. Not only is it the most abundant biopolymer in the world, but its good mechanical properties and easily modifiable functional groups make it an attractive alternative to conventional materials (Hokkanen et *al.,* 2016). Cellulose is known for its good mechanical stability and strength, providing good resistance for the material against harsh operation conditions and degradation from prolonged use. The porous nature of cellulose is another benefit. Porosity generates a large surface area, providing ample room for efficient contaminant removal (Akl et *al.,* 2023; Hokkanen et *al.,* 2016). Furthermore, the structure and surface morphology of cellulose (figure 2.7) is one of the biggest draws to its application as a biosorbent. Particularly, the hydroxyl and carboxyl groups are what facilitate interactions between the cellulose and contaminants in solution. Typically, this is done through hydrogen bonding and electrostatic interactions (Liu et *al.,* 2021; Suhas et *al.,* 2017).

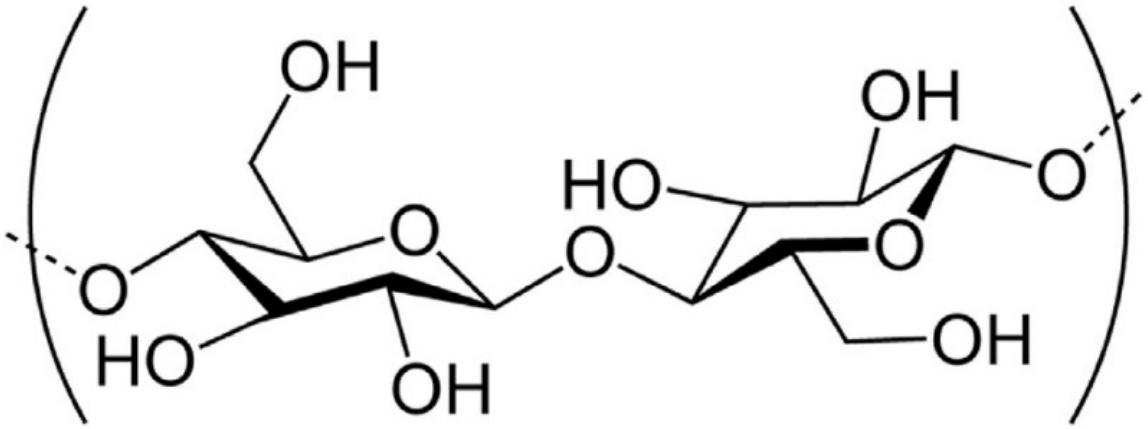

Fig. 2.7: Structure of cellulose. (Hokkanen et *al.,* 2016)

The modification of functional groups on the cellulose surface to improve the removal capacity of the material is what distinguishes cellulose from other biosorbents. Various methods exist, such as esterification, amination, and oxidation (Hokkanen et *al.,* 2016). Different methods will produce different surface characteristics and can be used to target certain contaminants. Esterification, for example, uses acid anhydrides to react with hydroxyl groups and convert them into carboxylic acid groups. This results in a surface with enhanced hydrophobic properties and improved organic pollutant removal characteristics (Boufi & Alila, 2011). On the other hand, oxidation introduces

carboxyl groups in place of the hydroxyl groups. This method produces greater hydrophilic characteristics as well as increased surface reactivity. In the case of TAN removal, this would be a preferred method as there is potential for electrostatic bonding, hydrogen bonding, or ion exchange between ammonia and these new functional groups (Ong et *al.,* 2022; Hokkanen et *al.,* 2016).

Kose et al. (2020), for example, applied cellulose nanofibrils (CNFs), which are long, fibrillated cellulose structures, for the removal of iron from aqueous solution. Results indicated that the oxidized cellulose showed favorable adsorption and was able to achieve adsorption capacities upwards of 8-10 mg/g.

2.3.1.2 Flax Fibre

Significant quantities of flax fibre are produced as agricultural waste products from the cultivation of flax seeds. Flax, a blue-flowered plant grown mainly in cool, northern climates, is an annual, high-yield crop that is low cost and easy to produce. Composed mainly of cellulose with some lignin and hemicellulose, the hydroxyl and carboxyl groups of cellulose, along with the flax superstructure, promote its sorption characteristics (Akl et *al.,* 2023; Mongiovi et *al.,* 2021). A major draw to this material is its abundance. Canada is a world-leading producer of flax seed, accounting for roughly 40% of production globally. In Canada, various byproducts of flax seed farming, such as flax straw, fibre, and shive, are underutilized and exist in copious amounts that can be used by other industries instead of being disposed. Furthermore, environmental concerns that arise with the disposal of these fibres, such as air pollution from burning practices, can be greatly reduced through the utilization of flax seed waste (Flax Council of Canada, 2019; Reaney et *al.,* 2006).

Work is currently being done with flax fibres in several fields, including use in composite materials, as reinforcement for concrete and other structural materials, and as a method of treatment for a range of contaminants such as heavy metals and dyes (Mongiovi et *al.,* 2021; Korniejenko et *al.,* 2020). For example, Foruzanmehr et al. (2017) looked at treatments for the improvement of fibres mechanical properties and the potential for flax to act as a replacement for glass fibres in engineering and composite materials. Others have looked at the treatment capabilities for flax fibres; studies have included even the removal and recovery of uranium from wastewater (Abutaleb et *al.,* 2020). Heavy metals are a particularly common contaminant, and several publications have outlined the potential for flax fibres to be applied to water treatment for lead, cobalt, cadmium, and zinc, as well as contaminants of organic

origin (Dey et *al.,* 2021; Mongiovi et *al.,* 2021; Abbar et *al.,* 2020). Ultimately, however, there is limited work relating to the use of flax fibres for the treatment of TAN laden wastewater.

2.3.2 TEMPO Oxidation

As mentioned previously, biosorbents containing cellulose are sought after for their modifiable surface functional groups that can be harnessed to improve performance. Oxidation, which in the case of cellulose describes the introduction of oxygen-containing functional groups, is one type of modification commonly applied to improve properties. Several methods exist for the oxidation of cellulose, such as sodium periodate and several types of metal oxidants. TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl)-mediated oxidation, however, is a preferred choice for its selectivity and operation under moderate conditions (Tang et *al.,* 2021; de Nooy et *al.,* 1995). Selectivity describes the process's ability to target and react to specific functional groups. High selectivity will support the material's structure and be much more efficient than a reaction with low selectivity. TEMPO-mediated oxidation is selective for several reasons, including steric hindrance due to the size of the TEMPO molecule, which limits its ability to access certain sites on the cellulose surface. Additionally, conditions such as co-oxidants, TEMPO concentration, and pH can be carefully controlled to promote selectivity by limiting overoxidation and side reactions (Tang et *al.,* 2021; Hokkanen et *al.,* 2018). An added benefit is that the conditions in which the reaction is undergone are moderate compared to other forms of oxidation. TEMPO-mediated oxidation can be implemented at room temperature, with the only limiting factor being a maintained pH of 10 throughout (Ong et *al.,* 2022).

The mechanism by which TEMPO-mediated oxidation modifies the surface of cellulose, as shown in Figure 2.8, is the selective oxidation of the C6 primary hydroxyl groups to sodium C6-carboxylate groups. This reaction is implemented as a system with sodium hypochlorite (NaClO) and sodium bromide (NaBr) working as the primary oxidant and co-catalyst, respectively (Isogai et *al.,* 2018; Saito et *al.,* 2007).

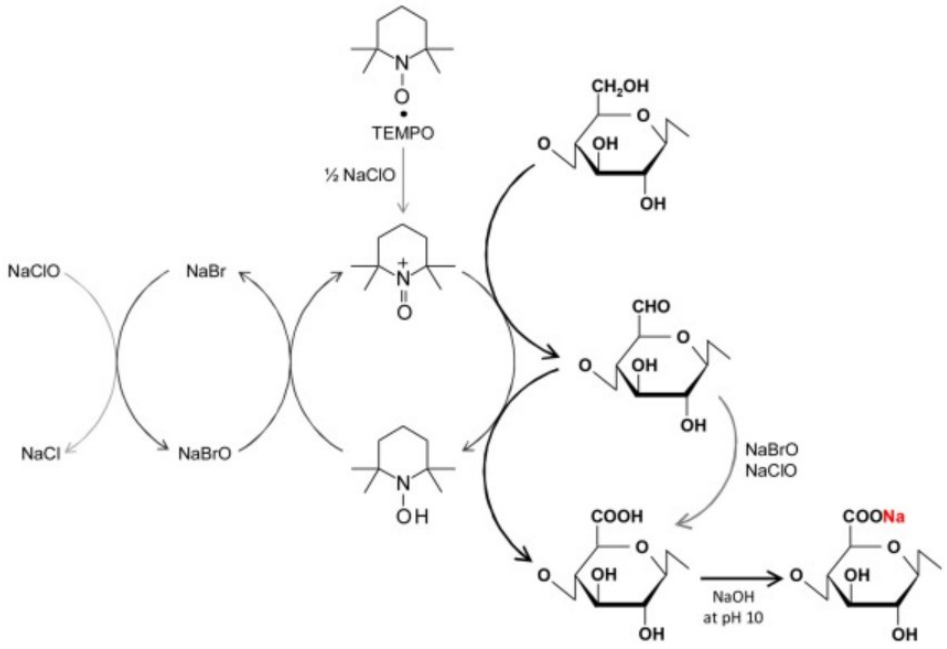

Fig. 2.8: Oxidation mechanism of cellulose by TEMPO-mediated oxidation. (Isogai et *al.,* 2018)

Extensive studies have been conducted on the conversion of hydroxyl to carboxyl groups in cellulose and have established a pathway to describe the modification. NaClO, acting as the primary oxidizer, will oxidize the TEMPO radical to $TEMPO^+$. The oxidized TEMPO radical reacts with the C6 hydroxyl to produce C6 aldehydes, which are finally converted into carboxyl groups through oxidation with NaClO and sodium hypobromite (NaBrO). Additionally, $TEMPO^+$ is itself oxidized during the process by NaBrO, leaving only NaClO to be consumed in the reaction (Ong et *al.,* 2022; Tang et *al.,* 2021; Isogai et *al.,* 2018).

2.4 Summary of Research and Knowledge Gap

Many methods for the removal of TAN from wastewater have been developed and improved upon over time, each with its own benefits and drawbacks. As opinions and standards on the environmental and economic impacts of water treatment continue to evolve, an interest in the development of alternative technologies that address these issues has grown. Ion exchange has proven to be an effective method of TAN treatment using zeolites and synthetic resins, though issues can arise regarding the disposal of exhausted materials after prolonged use. Also to be considered is the cost of producing these materials, which can be high compared to options like agricultural waste. Biosorbents, derived from agricultural waste, food waste, and microorganisms, among others, are a practical alternative to traditional ion

exchange materials. Many published works have investigated the use of materials including banana peels, rice straw, and wastepaper sludge for the treatment of contaminants such as dyes, heavy metals, or nitrates. An agricultural waste product of particular interest is flax fibre, which is in abundance as Canada is a world-leading producer of flaxseed and flaxseed oil. In addition to their availability, the cellulosic nature of flax fibres makes them a strong candidate for chemical treatments meant to improve their removal characteristics. The bulk of research done on the use of flax fibres for wastewater treatment covers the removal of heavy metals and dyes; therefore, this study will try to determine the impact of chemical modifications on the fibre's surface and the effectiveness of these modified fibres for the treatment of TAN. It will also look to analyse the possible mechanism of removal via spectroscopy methods.

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Chapter 3: Experimental Methods and Materials

This thesis aims to determine the impacts of pre-treatment and functionalization (i.e., TEMPO oxidation) on the adsorption capacity of the modified flax fibres for the removal of TAN from liquid phase. The research mainly consisted of several batch isotherm tests to establish the adsorption characteristics of the fibres under various conditions. Initial batch tests were run on as-received fibres to create a benchmark for the fibre's removal capacity. The following batch tests were conducted on fibres after they had undergone chemical pre-treatments and the TEMPO oxidation technique. Further batch testing was performed under varying conditions, including changes in the initial contaminant concentration, pH, and temperature.

In addition, the regeneration of fibres was conducted through various loading and unloading cycles. Lastly, samples of both as received and pre-treated/oxidized fibres underwent several surface imaging and characterization techniques. This was done to help establish the impacts of chemical pre-treatment and the effectiveness of the oxidation method.

3.1 Materials

3.1.1 Flax Fibres

Raw flax fibres were acquired from Biolin Research Incorporated (Biolin, Saskatoon, SK). Fibres were received in long, strangled bundles and contained some amounts of husk and straw, as seen in Figure 3.1. Additionally, Biolin noted that fibres were collected directly from processing and were not washed or otherwise treated before shipping.

Fig. 3.1: Flax fibres, as received.

3.1.2 Treatment and Oxidation Chemicals

Acetone of high-performance liquid chromatography (HPLC) grade and sodium hydroxide used in the pre-treatment phase were purchased from Fisher Scientific. The chemicals required to produce the TEMPO solution—sodium bromide, sodium hypochlorite, and TEMPO—were all purchased from Sigma-Aldrich. Chemicals were generally of American Chemical Society (ACS) grade to ensure elevated levels of purity.

3.1.3 Synthetic Ammonia Solution

A synthetic TAN solution was used for the batch adsorption testing in the form of an ammonium chloride solution. This solution was produced by dissolving 1.484 g of ACS-grade NH_4Cl, purchased from Fisher Scientific, into 1L of distilled water to produce a stock solution of 500 mg/L as NH_4^+. For testing, this stock solution was further diluted using deionized water to the desired concentrations.

3.2 Analytical Methods

3.2.1 Ammonia Analysis

The main method applied for the measurement of TAN concentrations was the Nesslerization Standards Method (Baird et *al.,* 2017), which utilizes a colour change reaction generated by the addition of Rochelle salt stabilizer and Nessler reagent to a TAN solution. Specifically, mercury, iodine, and potassium found in Nessler reagent react with TAN to generate a yellow-orange colour change in a reaction known as Nesslerization. Rochelle salt acts as a stabilizer to prevent any precipitate from forming in the solution (Baird et *al.,* 2017). The procedure involved adding 0.125 mL of Rochelle stabilizer to 10 mL of the ammonia solution with a known TAN concentration and mixing well before adding 0.1 mL of the Nessler reagent, again mixing well, and allowing the solution to react for 10 min. If TAN is present, the colour change reaction occurs, the intensity of which is directly proportional to the TAN concentration and can be determined based on light absorbance via a spectrophotometer (DR6000, HACH) at a wavelength of 425 nm. Prior to the analysis of the tested samples, a calibration curve was developed using samples with known concentrations. This was done by first zeroing the spectrophotometer through the analysis of a blank sample of de-ionized water with Rochelle salt and Nessler reagent added. The triplicated samples of standard solutions were analysed in two ranges: a low-end curve ranging from 1-6 mg TAN/L and a high-end curve ranging from

7-12 mg TAN/L. Applying the least squares method, the line of best fit was determined. Figures 3.2 and 3.3 show the calibration curves generated for the two ranges, along with the R^2 value and equation of the line.

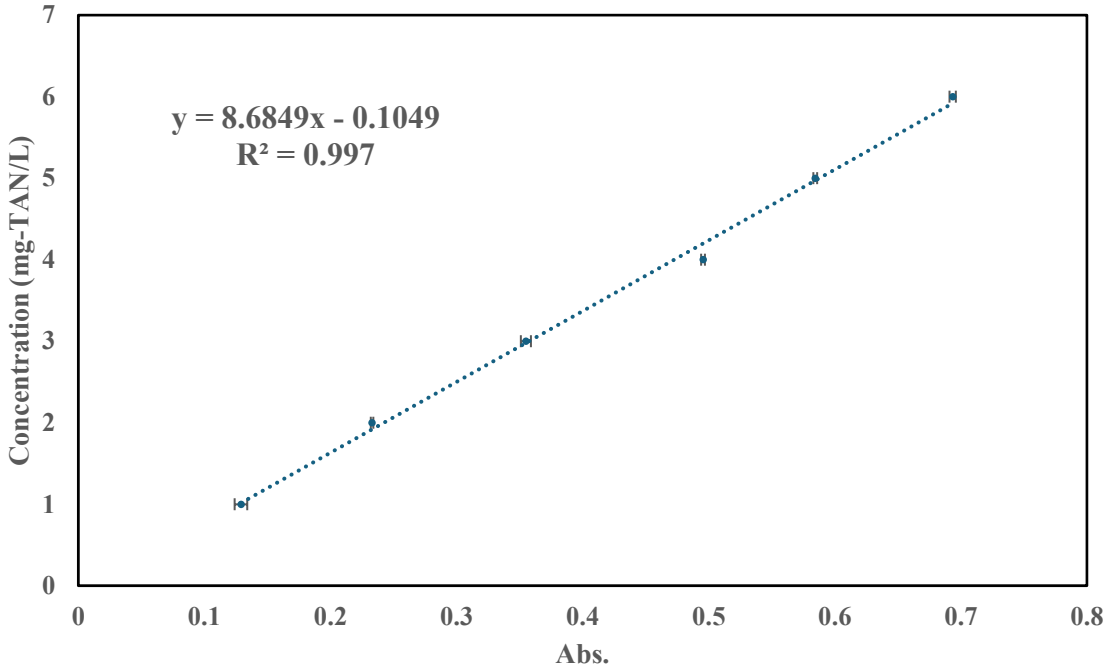

Fig. 3.2: Low-end concentration calibration curve for the Nessler method (based on the average of 3 replicates).

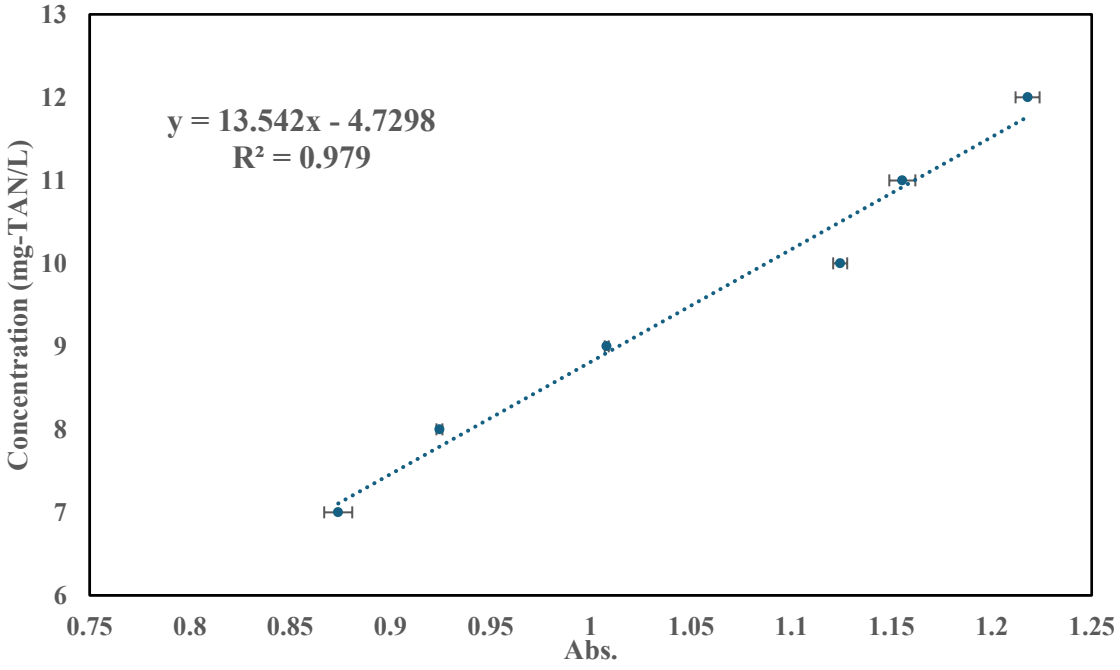

Fig. 3.3: High-end concentration calibration curve for the Nessler method (based on the average of 3 replicates).

In addition to Nessler method measurements, in some cases, measurements were supplemented or confirmed using Hach TNT-832 vials, a prepackaged salicylate method. This method follows a similar principle to the Nessler method, though in this case, ammonia reacts with hypochlorite and salicylate ions in the presence of sodium nitroprusside to produce a green-blue colour change, as shown in Figure 3.4 (TNT-832, HACH). As with the Nessler method, this colour change is proportional to the TAN concentration, and absorbance can be measured on the spectrophotometer at a wavelength of 650 nm. The procedure consists of adding 0.2 mL of TAN solution to the test vial and shaking it after screwing the cap on with the reagent powder able to mix into the solution. After 15 min to allow for the reaction to occur, the vial can then be analysed, which, in the case of this method, will return a direct value of the NH_3-N concentration. For the sake of consistency in TAN measurements with the Nessler method, the values of NH_3-N can be converted into NH_4^+ by multiplying by a factor of 18/14, the molecular weight fraction.

Fig. 3.4: Ammonia analysis methods; Ammonia solution after addition of Nessler reagent (left), HACH TNT-832 vials after the addition of ammonia solution (right).

3.2.2 pH

pH measurements were taken using a Hach pH probe (PHC101, HACH) connected to a portable pH meter (HQ40d, HACH). Stock buffer solutions (VWR chemicals) with pH values of 4.0, 7.0, and 10.0 were used in the calibration of the probe before each use.

3.2.3 Temperature

Temperature was recorded using the thermometer, which is part of the pH probe and pH meter (PHC101 and HQ40D, HACH). Temperature was also occasionally measured using an external mercury thermometer.

3.3 Experimental Methods

3.3.1 Fibre Treatment and Oxidation

To remove unwanted materials from the surface of the fibres before oxidation, the fibres underwent a two-step pre-treatment process (figure 3.5). Firstly, flax fibres were immersed in boiling acetone under reflux and remained there for 30 min. Secondly; after ensuring the fibres were dry, a 5% by-weight solution of sodium hydroxide was used to treat the fibres for a further 2 h. The flax was then immediately rinsed and submerged in distilled water, which was adjusted to a neutral pH using dilute hydrogen chloride to remove any remaining alkalinity. Then, the fibres were dried at 50^{o} C in an oven overnight. This process aimed to clear waxes, lignin, and hemicellulose that could be found on the fibres. As a result, the surface was more susceptible to the oxidation process (Foruzanmehr *et al.,* 2014).

The oxidation process, meant to convert existing hydroxyl groups into carboxyl groups, began with the preparation of a TEMPO solution. This was done by combining 0.484 g of sodium bromide and 0.414 g of sodium chloride in 100 mL of deionized water, which was followed by the addition of 0.02 g of the TEMPO oxidizer. The addition of dilute hydrochloric acid was required to decrease the basicity and bring the pH of the solution to 10; this was necessary to ensure that the reaction occurred efficiently. The fibres were immersed in the TEMPO solution and mixed gently for 60 seconds, after which they were removed and washed thoroughly with distilled water. The ratio of TEMPO solution used was 100 mL for every gram of cellulose present; in the case of flax fibres, this meant a ratio of 100 mL for every 1.4 g of treated flax fibres, as they were approximately 70% cellulose (Fathi et *al.,* 2019). Oxidation was carried out in fibre bundles of 0.5 g to maximize contact between the flax surface and the TEMPO solution. Finally, after the fibres were properly rinsed, they were left to dry in an oven at 50^{o} C overnight.

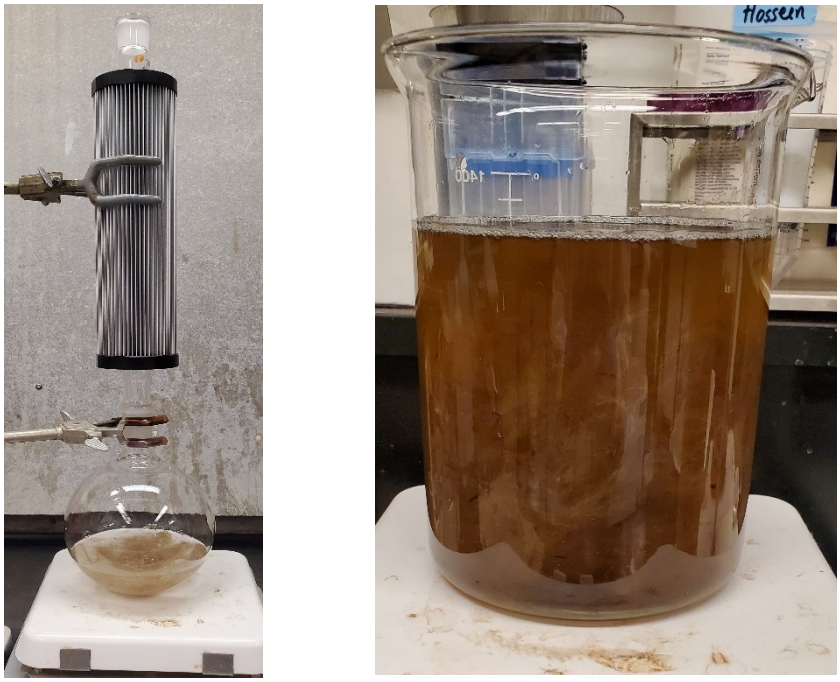

Figure 3.5: Acetone treatment setup (left) and alkali treatment setup (right)

3.3.2 Kinetic Experiments

Establishing the time required for the fibres to reach equilibrium was done by performing kinetic experiments with pre-determined contact time intervals. Tests were conducted in 250 mL Erlenmeyer flasks under the following conditions, which were the same for every sample: 50 mL of TAN solution, TAN concentration of 50 mg/L, and an adsorbent dose of 0.5 g. A blank sample of deionized water and a control containing only TAN solution were included as well. All flasks were placed on an orbital shaker at 150 rpm and were designated various contact times ranging from 5 min to 24 h. After reaching its allocated time, the flask was removed, and the solution was vacuum filtered from the flax fibres to measure the TAN concentration and to check temperature and pH levels.

In addition, the pseudo-first order and pseudo-second order kinetic models were chosen to model the results for their good fitting quality and applicability. These models are defined as follows:

Pseudo-first order: $$q_t = q_e(1 - e^{-kt}) \quad \text{(eq. 3.1)}$$

Pseudo-second order: $$q_t = \frac{k_2 \cdot q_e^2 \cdot t}{1 + k_2 \cdot q_e \cdot t} \quad \text{(eq. 3.2)}$$

Where q_t is uptake capacity at time t (mg/g), q_e is the equilibrium uptake capacity (mg/g), t is the contact time (min), and k and k_2 are the rate constants of the pseudo-first order and pseudo-second order models, respectively.

3.3.3 Batch Adsorption Testing

Batch adsorption testing was conducted by performing several isotherms, a constant temperature test used to determine the TAN uptake capacity of a material in a closed environment. Tests were conducted by adding 50 mL of TAN solution, with various concentrations, into 250 mL Erlenmeyer flasks. Treated flax fibres were then weighed and distributed into each flask (Figure 3.6). Flasks were covered and placed in an orbital shaker overnight to ensure that equilibrium was reached. After 24 h of agitation, samples were separated through 47 nm microfibre filters, and the Nesslerization method outlined earlier in the chapter was used to determine the final TAN concentration. In each test, blank flasks containing distilled water and flax fibres, as well as control flasks containing only TAN solution, were used. This was done to establish any contamination that may come from the fibres themselves or if any issues with volatilization during the test may be a factor, respectively. In addition, all samples were made in triplicate to improve the accuracy of the results. Equilibrium solid phase concentrations, or uptake capacity, were calculated using the mass balance of the reaction based on the following equation:

$$q_e = \left(\frac{C_o - C_e}{w}\right) \cdot V \qquad \text{(eq. 3.3)}$$

Where q_e is the uptake capacity (mg contaminant/g media), C_0 and C_e represent the initial and equilibrium concentration (mg/L), respectively, w is the adsorbent dose (g), and V is the volume of the sample solution (L). The resulting data can then be plotted by applying isotherm models, such as Langmuir and Freundlich, in the form of q_{eq} vs. C_{eq}.

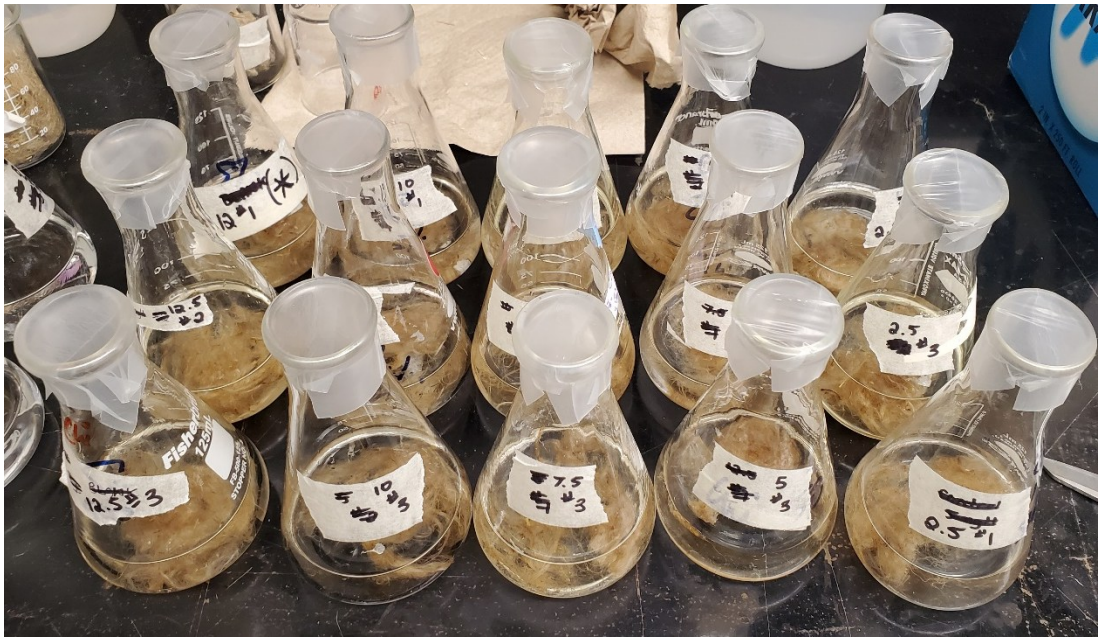

Figure 3.6: Oxidized flax fibre samples in flasks.

3.3.4 Regeneration

Regeneration studies were conducted using NaCl solutions of varying concentrations, along with regeneration using deionized water to evaluate the response to repeated loading and measure any ions leached from the fibres. The NaCl regeneration solutions consisted of 5% and 10% by-weight mixtures made by adding 50 g and 100 g of NaCl to 1 L of water, respectively.

Samples first underwent batch tests following the procedure previously outlined. After undergoing the first round of testing, samples were removed from the TAN solution and gently rinsed before being placed in the various regeneration solutions. Samples were placed in an orbital shaker and left for 24 h after which they were separated from the regeneration solution, rinsed, and then placed back in a TAN solution to begin the second cycle. TAN concentrations, along with pH and temperature, were monitored to determine the impacts of several regeneration cycles on these parameters. Based on the volume of solution and concentrations after regeneration, the mass of the contaminant can be determined using the following equation:

$$Mass\ of\ Contaminant = Concentration \cdot Volume \quad \text{(eq. 3.4)}$$

Where mass of the contaminant is in mg, the concentration is mg/L, and the volume is in L. Conducting a mass balance over the system allows for the quantification of contaminant removed during the initial loading phase and then how much contaminant was released during the regeneration phase. For each NaCl concentration and control, samples were tested in triplicate and underwent three loading-regeneration cycles.

3.3.5 Materials Characterization Techniques

SEM analysis was conducted on fibers before and after pre-treatment and on a sample after oxidation. Imaging was carried out at the materials testing laboratory at Carleton University. This was done with a Tescan Vega-II XMU scanning electron microscope at 10 kV and a working distance of 10 mm. XPS and FTIR analysis was also conducted to inspect in more detail the properties and chemical profile of the surface of the flax fibres after oxidation. XPS was conducted with a Kratos Axis Ultra spectrometer using a monochromatic Al source. FTIR analysis was performed using a JASCO-4600 spectrometer with a range of 600 cm^{-1} to 4000 cm^{-1} at a resolution of 4 cm^{-1}. XPS and FTIR characterization was carried out at the Materials Research and Analysis Platform at Sherbrooke University.

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Chapter 4: Ammonia Removal from Aqueous Solution Using Novel Biosorbent Developed from TEMPO Oxidized Flax Fibres

Abstract

Ammonia is a significant environmental pollutant, and this study explores the use of flax fibres, a sustainable agricultural waste, for its removal. Fibres underwent chemical treatment to eliminate non-cellulosic matter and increase exposure of functional groups and were subsequently oxidized using TEMPO-mediated oxidation. Surface characterization methods, including scanning electron microscopy, x-ray photon spectroscopy, and Fourier transform infrared spectroscopy, indicated successful treatment, showing the removal of surface extractives and the presence of new functional groups. Batch adsorption tests showed adsorption capacity improved from 0.912 mg/g using unmodified fibres to 3.373 mg/g following chemical modification, indicating approximately 270% increase, with optimal TAN uptake at pH 6-7. Both the Langmuir (R^2 = 0.981, RMSE = 0.064) and Freundlich (R^2 = 0.980, RMSE = 0.066) models described the experimental data well, and chemisorption was suggested as the removal mechanism based on the pseudo-second order kinetic model (R^2 = 0.998). Thermodynamic analysis indicated the removal process as being endothermic and non-spontaneous under the conditions tested. Regeneration tests demonstrated 87% retention in adsorption capacity when using a 10% NaCl regenerant solution over three cycles. This study demonstrates the potential of flax fibres as an eco-friendly, cost-effective material for TAN removal, highlighting its potential applicability in sustainable wastewater treatment technologies.

Keywords: Ammonia adsorption, TEMPO oxidation, Flax fibres, Biosorbents, Thermodynamic Analysis, Surface characterization, Sustainable wastewater treatment

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4.1 Introduction

A contaminant of concern in water resources is ammonia nitrogen, often found in chemical fertilizer runoffs, mine tailings, and other industrial wastewaters (Adam et *al.,* 2019). Harmful effects of discharged ammonia include eutrophication, depletion of dissolved oxygen, toxicity to aquatic organisms, and the potential for contamination of groundwater sources (Segura et *al.,* 2019; Dey et *al.,* 2021). In the aquatic environment, ammonia exists in two forms: ionized ammonia (NH_4^+) and its unionized form (NH_3). The combined concentrations of these two forms are often reported as total ammonia nitrogen (TAN) (Ding and Sartaj, 2016). Concentrations of TAN in wastewaters can range from a few mg/L to over 1000 mg/L, depending on the source (Farghali et *al.*, 2024; Back et *al.*, 2023). Based on the statistics from National Pollutant Release Inventory (NPRI), the majority of ammonia releases in Canada in 2019 were releases to water (50,400 tonnes out of a total of 69,400 tonnes) (NPRI, 2024). The Canadian Council of Ministers of the Environment has established a value of 0.019 mg/L of unionized ammonia as the upper limit for freshwater bodies (Environment Canada, 2010). Additionally, discharge limits in Canada are established under the Fisheries Act and are determined based on acute lethality level testing (Minister of Fisheries and Oceans of Canada, 2012).

Various methods exist for the removal of TAN from aqueous phase, including ion exchange, air stripping, and biological treatment (nitrification-denitrification) (Almutairi and Weatherley, 2015; Cao et *al.,* 2021; USEPA, 2000). Biological treatment has been one of the most widely implemented methods worldwide; however, due to its sensitivity to temperature, heavy metals, and very high TAN concentrations, it can run into complications. This can impact operations, particularly in colder parts of Canada or with certain types of industrial wastewater effluents (Narbaitz et *al.,* 2020; Almutairi and Weatherley, 2015; Ding and Sartaj, 2015). As a result, it can be an expensive, ineffective, and impractical process that requires elevated levels of monitoring. Similarly, air-stripping suffers performance issues from temperature changes, including the risk of exposed wastewater freezing at very low temperatures. Furthermore, the process must be conducted at high pH values, as ammonia must be in the NH_3 form for this method (USEPA, 2000). Conversely, other physical and chemical methods, such as the adsorption and ion exchange techniques, can be implemented to avoid these problems (Seruga et *al.,* 2019). Advantages include simple and inexpensive operation, as well as limited impact from extreme temperatures and shock loading (Du et *al.,* 2005; Narbaitz et *al.,* 2023). The adsorption and ion exchange processes have received more interest in recent years because of these factors. Discovering efficient and low-cost materials for this process has been a major focus in the industry, and various studies have shown that zeolites and activated carbons are examples of economic and effective materials

(Han et *al.,* 2021; Narbaitz et *al.,* 2020). These materials, however, need to be mined or produced synthetically. This has generated interest in the use of low-cost alternative sources, like agricultural waste, which can be seen as a more sustainable alternative (Jagaba et *al*., 2020; De Gisi et *al.,* 2016). This will allow for a decrease in total waste volumes (for both the waste source and treatment facilities), limit the production of hazardous byproducts, and further lower costs (Li et *al*., 2019; De Gisi et *al.,* 2016). Cellulose-based waste products, such as flax fibres, are promising for this application due to their abundance, strong mechanical properties, and versatility towards chemical modifications (Ong et *al.,* 2022). Canada is one of the top producers of flax seed in the world; Saskatchewan alone accounts for one-third of flax produced globally (Prairie Clean Energy, n.d.). As such, there is interest in expanding the application of cellulosic materials for TAN treatment by using flax bast fibres, which are generated in copious amounts in Canada and are currently discarded or burned. A current focus on cellulose modification for treatment processes involves the oxidation of surface hydroxyl groups into carboxyl groups (Figure 4.1). This enhances the fibres' effectiveness for TAN removal by increasing surface reactivity and affinity. Oxidation provides increased availability of binding sites and specific binding sites for ionized ammonia (NH_4^+), whose lone electrons on nitrogen form hydrogen bonds with the structure of the carboxyl group. Additionally, the higher surface charge of the sodium carboxylate enhances electrostatic interactions, which can facilitate further attachment, and they are ionizable, allowing for ion exchange interactions with ammonium (Ong et *al.,* 2022; Isogai et *al.,* 2018; Isobe et *al.,* 2013). Oxidation via the TEMPO radical is seen as a viable method used in this procedure (Foruzanmehr et *al.,* 2014). Shown in Figure 4.1, NaClO oxidizes the TEMPO radical to the oxoammonium ion ($TEMPO^+$), which then selectively oxidizes the C6 hydroxyl groups to C6 aldehydes. These aldehydes are subsequently converted into carboxyl groups through further oxidation by NaClO, with NaBr acting as a mediator (Ong et *al.*, 2022; Isogai et *al.*, 2018). TEMPO is preferred over other oxidizers for several reasons, including its highly selective nature under appropriate conditions, which targets the C6 hydroxyl group and has a minimal impact on the remaining cellulose structure. Additionally, TEMPO oxidation is conducted in mild conditions relative to other methods, again limiting structural damage to the fibres, and it is a controlled process, allowing for greater precision over the amount of modification. Earlier research regarding this oxidation process via TEMPO on various cellulosic materials as well as flax fibres has observed the resulting adsorption of contaminants like heavy metals, dyes, and other contaminants (De Gisi et *al.,* 2016; Hokkanen et *al.,* 2016; Hubbe et *al.,* 2011). Results have shown several positives: chemical modifications do indeed improve adsorption capacities, and reasonable adsorption capacities can be achieved relative to conventional adsorbents (Ong et *al.,* 2022).

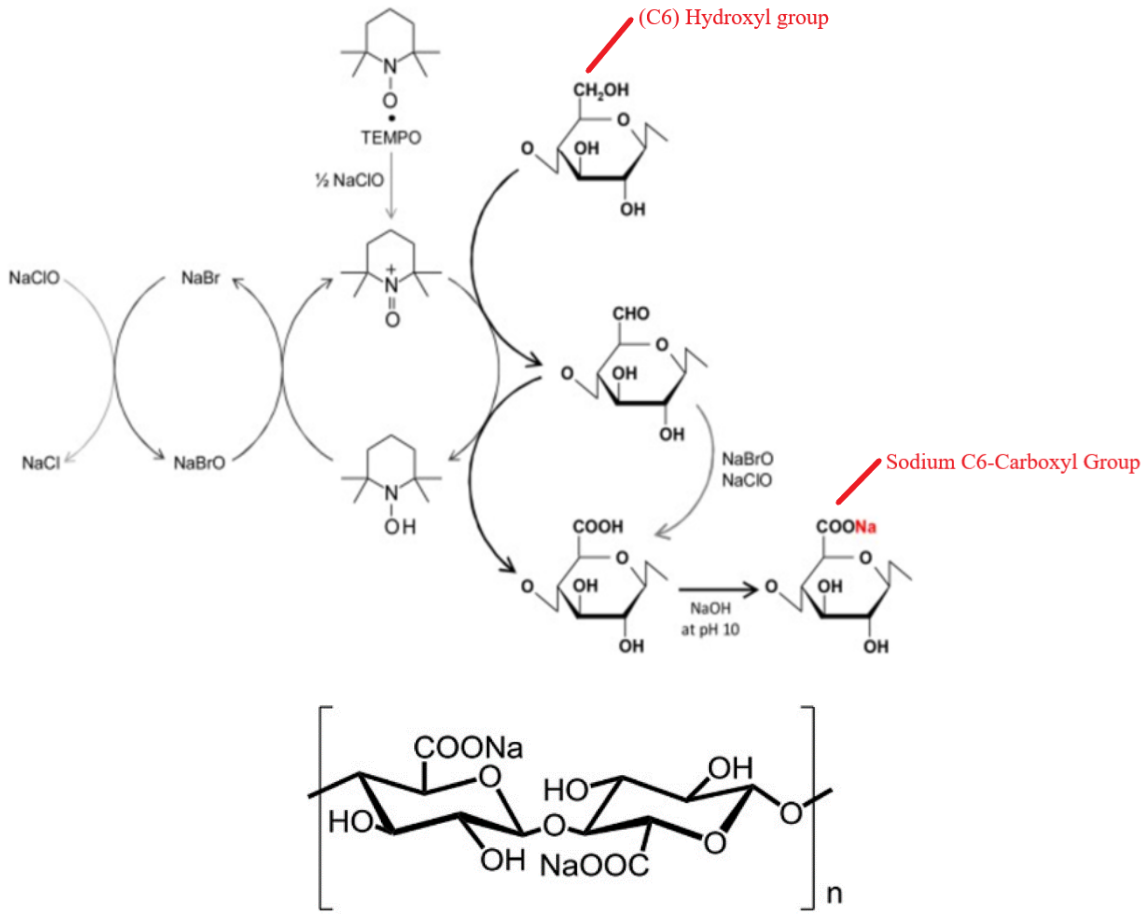

Figure 4.1: Oxidation mechanism of cellulose by TEMPO-mediated oxidation (top) and structure of cellulose unit after oxidation (bottom) (Isogai et *al.,* 2018).

Considering the above factors, the main goals of this study were to assess the efficiency of the chemical treatment processes for both the initial chemical treatment to expose the flax fibre's cellulose structure and the oxidation phase for functionalizing the surface. The effectiveness of flax fibre on the removal of TAN was further studied via batch adsorption tests, and the impacts of various test conditions, including TAN concentrations, pH, and temperature, were also determined.

4.2 Experimental Methods and Materials

4.2.1 Materials

Raw flax fibres were provided by Biolin Research Incorporated (Biolin, Saskatoon, SK). Treatment chemicals, including acetone (HPLC grade), sodium hydroxide (NaOH), and hydrogen chloride (HCl), were purchased from Fisher Scientific. TEMPO, sodium bromide (NaBr), and sodium hypochlorite were acquired from Sigma-Aldrich. Ammonium chloride, used to prepare the synthetic TAN solution, was purchased from Fischer Scientific. Furthermore, Rochelle salt and Nessler's reagent required for the Nessler method analysis were purchased from RICCA Chemical.

4.2.2 Flax Fibre Pre-treatment

After the manual removal of shiv and other undesirable remnants in the fibre bundles, pre-treatment of the fibres consisted of a two-step process, following the methodology outlined in Foruzanmehr et al. (2014). Firstly, flax fibres were submerged in boiling acetone under reflux for 30 min to remove surface impurities like waxes. The fibres were removed from the acetone and left to air-dry before undergoing alkaline treatment. The fibres were then submerged in a 5% by-weight solution of sodium hydroxide, which will remove lignin and hemicellulose that can also be found on the surface of the fibres, further preparing them for oxidation. Alkaline treatment proceeded for 2-h to improve cellulose exposure, up from 45 min often reported in prior research, which is used to aid the preservation of mechanical properties. Minor preliminary tests determined that a 2-h submersion time led to improved removal characteristics without compromising the structural integrity of the fibres. Upon removal from the alkali solution, the fibres were then immediately rinsed and submerged in distilled water, which was adjusted to a neutral pH using dilute hydrogen chloride to remove any remaining alkalinity. Finally, the fibres were dried at 50 ^{0}C in an oven overnight.

4.2.3 Flax Fibre Oxidation

The oxidation process, meant to convert existing hydroxyl groups into carboxyl groups more capable of interacting with the contaminant, begins with the preparation of a TEMPO solution. This is done by combining 0.484 g of sodium bromide and 0.414 g of sodium chloride in 100 mL of de-ionized water, which is followed by the addition of 0.02 g of the TEMPO oxidizer (Foruzanmehr et *al.,* 2014). The solution is stirred, and the pH was decreased slightly to a value of 10 through the addition of dilute hydrochloric acid. For every 1 g of flax fibre to be oxidized, 100 mL of the TEMPO solution were prepared. The oxidation procedure, however, was conducted using 0.5 g of fibres at one

time to limit crowding in the glassware and maximize surface contact. Pre-treated fibres were submerged in the TEMPO solution for 60 s at 23 ^{0}C and then thoroughly rinsed with distilled water after removal. Oxidized fibres were then left overnight to dry in an oven at 50 ^{0}C, at which point they were ready for batch adsorption testing.

4.2.4 Materials Characterization Techniques

Materials characterization was performed for analysis of the surface morphology and chemistry of the flax fibres before and after treatment and oxidation as well as after batch testing. SEM analysis was done on fibres as received, on fibres having undergone pre-treatment, and on fibres having undergone oxidation. Imaging was performed in the materials testing laboratory at Carleton University with a Tescan Vega-II XMU scanning electron microscope, set to 10 kV, with magnifications of 300x or 2000x and a working distance of 10 mm. Imaging was performed using secondary electron detection as well as backscattered electron detection.

FTIR and XPS analysis was also conducted to inspect in more detail the properties and chemical profile of the surface of the flax fibres after oxidation. FTIR was done using a JASCO-4600 spectrometer with a range of 600 cm^{-1} to 4000 cm^{-1} at a resolution of 4 cm^{-1}. XPS survey scans and high-resolution analysis were performed using a Kratos Axis Ultra spectrometer with a monochromatic Al source. FTIR and XPS testing was conducted at the Materials Research and Analysis Platform at Sherbrooke University.

4.2.5 Analytical Methods

Concentrations of TAN in solution were measured by the Nesslerization Standard Method 4500-NH_3 (Baird et *al.,* 2017) with the aid of an Hach DR6000 spectrophotometer. The amount of contaminant adsorbed per unit mass of the adsorbent, also known as uptake capacity (q_e, mg/g), as well as the removal percentage, were calculated using the following equations:

$$q_e = \left(\frac{C_o - C_e}{w}\right) \cdot V \qquad \text{(eq. 4.1)}$$

$$Removal\ \% = \left(\frac{C_o - C_e}{C_o}\right) \cdot 100 \qquad \text{(eq. 4.2)}$$

Where q_e is the uptake capacity (mg contaminant/g media), C_0 and C_e represent the initial and equilibrium concentrations (mg/L), respectively, w is the adsorbent dose (g), and V is the volume of the sample solution (L).

All isotherms were modelled with the Langmuir isotherm model:

$$q_{eq} = \frac{b \cdot Q_{max} \cdot Ceq}{1 + b \cdot C_{eq}} \quad \text{(eq. 4.3)}$$

Where q_{eq} is the equilibrium solid phase concentration (mg contaminant/g media), b is the Langmuir constant (L/mg), Q_{max} is the maximum adsorption/exchange capacity (mg/g), and C_{eq} is the equilibrium phase concentration (mg/L). This model applies several assumptions: Adsorption occurs in a single layer (monolayer) on the media surface; there are a finite number of identical sites available for exchange or adsorption; and there will be no interaction between ions once they occupy a site (El-Sawaf et *al.*, 2024; Ayawei et *al.*, 2017).

In addition, isotherms were modelled using the Freundlich isotherm model:

$$q_{eq} = K_F \cdot C_{eq}^{\frac{1}{n}} \quad \text{(eq. 4.4)}$$

Where q_{eq} is the equilibrium solid phase concentration (mg contaminant/g media), K_F is the Freundlich adsorption constant (L/mg), C_{eq} is the equilibrium phase concentration (mg/L), and $1/n$ is the Freundlich exponent. Differences compared to the Langmuir model include the assumptions that the surface is non-uniform with various adsorption mechanisms and that there is the possibility of multilayer adsorption and exchange (Kalam et *al.*, 2021; Ayawei et *al.*, 2017).

A HACH PHC101 pH probe connected to a portable HQ40D pH meter was utilized for pH measurements throughout. Before use, the probe was calibrated using stock buffer solutions (VWR chemicals) with pH values of 4.0, 7.0, and 10.0. Additionally, temperature was measured using the thermometer built into the pH probe and meter. Temperature was also occasionally measured using a mercury thermometer.

4.2.6 Kinetic Experiments

Kinetics studies were performed to determine the time required for the adsorption of TAN to reach equilibrium. This was conducted using Erlenmeyer flasks containing 50 mL of ammonia solution with a TAN concentration of 50 mg/L and dosed with 0.5 g of oxidized fibres. Once prepared, flasks were placed on an orbital

shaker set at 150 rpm. Flasks remained shaking for a predetermined amount of time ranging from 5 min to 24 h. When a flask reached its designated contact time, it was removed from the shaker, and the solution was vacuum filtered to separate the fibres, at which point the TAN concentration was measured. Testing also included the addition of blank samples containing only deionized water and control samples containing only the TAN solution. The pH and temperature were also measured, and experiments were conducted at room temperature.

The pseudo-first order and pseudo-second order kinetic models were applied to the results of the kinetic experiments. These models were chosen for their good fitting quality and applicability to most adsorption data. The linearized form of each model is defined as follows:

Pseudo-first order: $$\ln\left(q_e - q_t\right) = ln(q_e) - k_1 \cdot t \quad \text{(eq. 4.5)}$$

Pseudo-second order: $$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \quad \text{(eq. 4.6)}$$

Where q_t is uptake capacity at time t (mg/g), q_e is the equilibrium uptake capacity (mg/g), t is the contact time (min), and k and k_2 are the rate constants of the pseudo-first order and pseudo-second order models, respectively.

4.2.7 Batch Adsorption Testing

Lab-scale batch adsorption testing was performed at several stages during the treatment and oxidation of fibres to compare the impacts these processes have on the removal efficiency of the fibres. Tests were conducted using 250 mL Erlenmeyer flasks containing 50 mL of an ammonium chloride solution adjusted to TAN concentrations ranging from 1 to 100 mg/L. Flax fibres were then distributed in solution, with masses typically ranging from 0.25 to 1.5 g. Flasks were placed on an orbital shaker and left for 24 h at 150 rpm to ensure equilibrium was reached, with each concentration typically replicated three times to improve the accuracy of the results. In addition, each test also included blank and control samples for detecting contamination or a decrease in TAN concentration from other sources, respectively. Vacuum filtration through 47-nm microfibre filters was then used to separate the liquid solution from the fibres for analysis. Experiments, unless otherwise specified, were carried out at room temperature (22-24 ^{o}C), and solution pH was not adjusted, typically remaining neutral or slightly above neutral. Three separate phases along the treatment and oxidation process were chosen for testing. Firstly, fibres were tested as received, then studies were conducted with fibres being subject to acetone and alkali treatments only, and lastly, testing was performed on

fibres that underwent both treatment processes and oxidation. Additional tests were performed to determine the effects of adjusting pH and temperature on the adsorption process. Tests involving temperature change were conducted in a cold storage room at 4 ºC to simulate conditions like those found in colder climates. Furthermore, tests were conducted over a range of pH values from 5 to 9 via the addition of dilute sodium hydroxide or hydrogen chloride to increase or decrease the pH, respectively. pH values were measured with a HACH Instruments pH probe and HQ40D meter.

4.2.8 Regeneration

NaCl solutions with concentrations of 5% and 10% by weight, along with control solutions of deionized water, were used as the regenerants during this phase of testing. Parameters to be considered include the effectiveness of each solution on the regeneration and leaching potential of the flax fibres and the impacts on the material's capacity after repeated loading and unloading cycles. Firstly, samples were handled following the previously outlined batch test procedure, using 0.5 g of fibre in 50 mL of TAN solution and shaken for 24 h, in what is known as the loading phase. Once loaded, samples were removed and gently washed with deionized water before being moved into the regeneration solutions. Regenerant solutions were prepared beforehand and distributed into flasks accordingly. The regeneration phase was accomplished in a comparable manner to the loading phase, with flasks being placed on an orbital shaker and allowed to mix for a further 24 h to maximize desorption. The combination of these two phases is referred to as a regeneration cycle. In the case of all regeneration samples, flasks were filled until full to minimize any volatilization of TAN in the solution and sealed to ensure no leaking or spilling occurred. Additionally, to determine the impacts that the regeneration cycle may have on other parameters in the system, parameters such as pH and temperature were monitored during the process.

To determine the TAN uptake during the loading phase and release during the regeneration phase, a mass balance before and after the regeneration cycle can be calculated by applying the uptake capacity equation (eq. 4.1). Three cycles were completed for each sample, with each solution being tested in triplicate to improve the accuracy of the results.

4.3 Results & Discussion

4.3.1 Surface Characterization of Fibres

4.3.1.1 Surface Chemical Properties (FTIR)

The FTIR spectra of oxidized fibres, both before and after undergoing testing conditions, are shown in Figure 4.2. Results show characteristic peaks found with cellulose: a large band from ~3500-3000 cm^{-1} associated with the hydroxyl groups of cellulose and O-H stretching; peaks in the range of ~1400-1300 cm^{-1} correspond to C-H bending vibrations as well as CH_2 wagging; and a large peak at ~1000 cm^{-1} attributed to the stretching vibrations of the primary and secondary hydroxyl groups found in the cellulose structure (Dhinesh et *al.*, 2024; Nazri et *al*., 2023; Panaitescu et *al.,* 2020). Confirmation of a successful oxidation can be established by looking for peaks at ~1600 cm^{-1} and ~1400 cm^{-1} which are characteristic of OH stretching and the COO^- asymmetric stretching of the C6-carboxylate groups (Ragab et al., 2024; Ong et al., 2022). The appearance of these peaks in Figure 4.2 would indicate the presence of C6-carboxylate groups on the surface of the fibres, and the results agree with previous studies conducted on the characterization of non-treated versus oxidized fibres (Nazri et *al*., 2023; Ong et *al.,* 2022; Panaitescu et *al.,* 2020). Furthermore, from the loaded samples, a decrease in the peak at 1400 cm^{-1} is indicative of the attachment of ionized ammonia molecules, limiting the peak corresponding to the carboxylate. A decrease in peak intensities was also seen for most peaks after loading of the sample, possibly owing to some decomposition of the fibres during the loading procedure (Ong et *al.,* 2022).

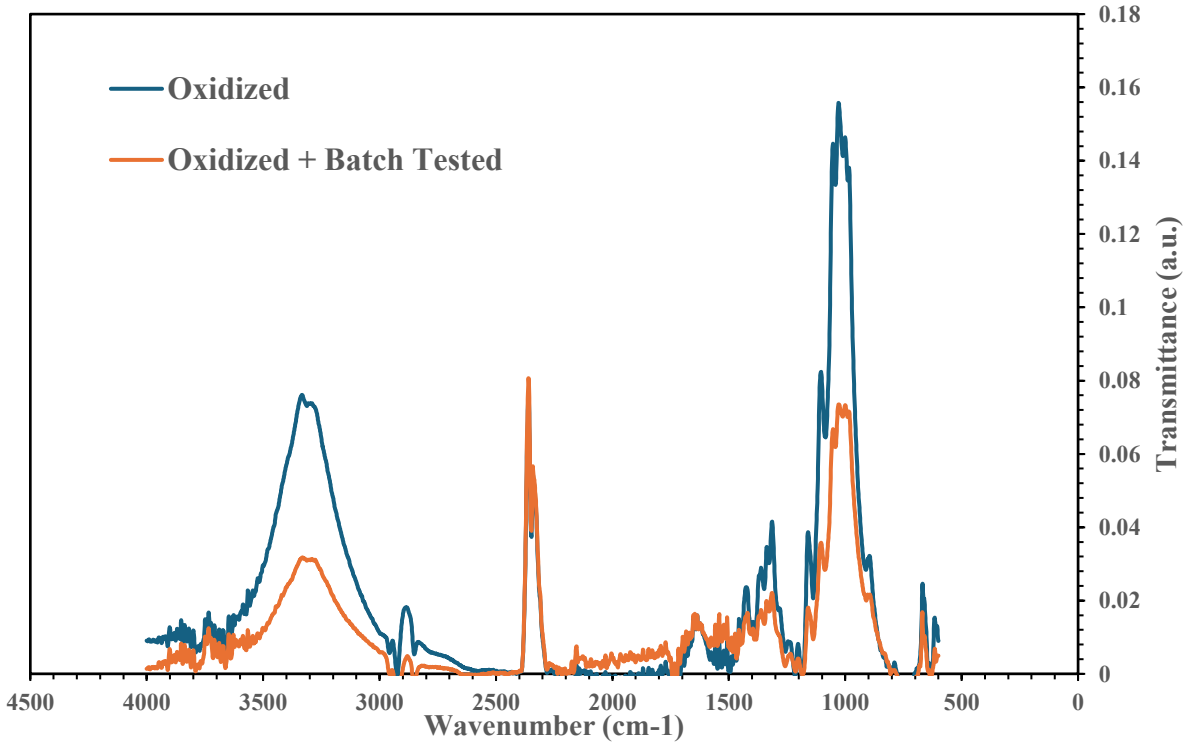

Figure 4.2: FTIR spectra of oxidized fibres and oxidized fibres after testing.

4.3.1.2 Surface Chemical Properties (XPS)

For a greater understanding of the chemical profile on the surface, XPS analysis was also conducted on oxidized fibres before and after undergoing batch testing. The full XPS survey spectra are shown in Figure 4.3. Peaks at 285.3 and 532.3 eV corresponding to carbon and oxygen, respectively, are also characteristic of the basic cellulose structure (Ong et *al.,* 2022). In addition, the oxygen/carbon ratio of the oxidized fibres was found to be ~0.5 (Table 4.1), which is a strong indication of the removal of extractives, as compared to several studies characterizing flax fibres, where the O/C ratios of non-treated fibres are typically found to be ~0.25 (Boulos et *al.,* 2017). The XPS spectra of C1s peaks, shown in Figure 4.4, characterize carbon bonding on the surface of the fibres. The spectra are divided into sub-peaks representing different bonds: C-C/C-H (C1) at 284.8 eV, C-O/C-N (C2) at 286.4 eV, C=O (C3) at 287.6 eV, COO (C4) at 288.5 eV, and COO^- at 289.6 eV. Firstly, it is observed that the C2 peak associated with the hydroxyl groups on cellulose is the largest and greater than C1, which is a strong indicator of successful oxidation treatment. This is a result of the C1 peak corresponding to hydrocarbon bonds found in extractives on the surface, such as wax and lignin, which has been shown to be the largest peak in several studies on non-treated fibres (Ong et *al.,* 2022; Panaitescu et *al.,* 2020; Boulos et *al.,* 2017). Furthermore, peaks found at 288.5 eV and 1071.3 eV, associated with O-

C=O and Na 1s, respectively, are also both strong indicators of successful oxidation by TEMPO. The appearance of O-C=O bonds along with the presence of sodium on the fibres surface would be because of the presence of sodium carboxylate on the fibre's surface and would not be found in non-treated samples (Panaitescu et *al.,* 2020; Zhu et *al.,* 2017).

A sample regenerated in a 10% sodium solution was also characterized using XPS to compare with the samples before testing. Results indicated that the surface chemistry was similar to samples before testing; however, indications of residual TAN and sodium were found, as evidenced by increased nitrogen percentages. Table 4.1 shows the regenerated sample has a lower O/C ratio due to a lower presence of oxygen. Relative to the oxidized sample, there was an increase in the relative atomic concentrations of nitrogen and sodium found on the survey spectra. This increase could be an indication of TAN remaining attached to the surface of the fibers and sodium from the regenerant solution. In addition, regenerated samples showed a decrease in the relative atomic concentration of the C4 peak when compared to the oxidized sample, down from 8.4% to 6.1%. As this peak is associated with the carboxylate groups on the surface of the fibres, TAN molecules still attached to these sites provide a possible explanation for this difference.

The findings from both FTIR and XPS analyses indicated the successful removal of most extractives from the flax fibre's surface. Results indicate the presence of bonds associated with non-cellulosic materials is lower than typically found on non-treated fibres, as well as an improved O/C ratio brought on by the removal of these extractives. Further analysis also seems to strongly suggest that fibres were successfully oxidized by TEMPO, with indicators such as the presence of sodium and bonds associated with the existence of sodium carboxylate.

Table 4.1: Relative atomic percentages and O/C ratio of non-treated, oxidized, and regenerated fibres.

Condition of Flax Fibres	N (%)	C (%)	O (%)	O/C	C4 Peak (O-C=O)	Reference
Non-treated	-	77.54	17.84	0.23	2.01	(Boulos et *al.,* 2017)
Oxidized	1.70	65.80	32.20	0.49	8.40	This Study
Regenerated	3.10	65.80	30.70	0.47	6.10	This Study

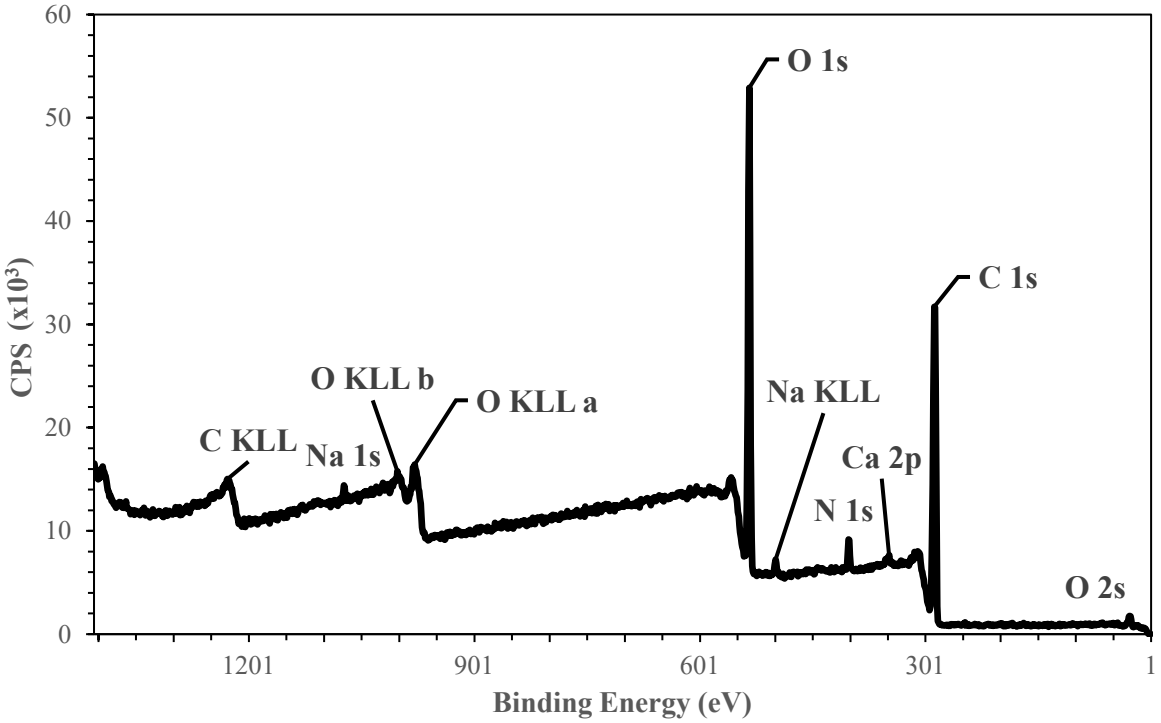

Figure 4.3: XPS survey spectra of oxidized fibres.

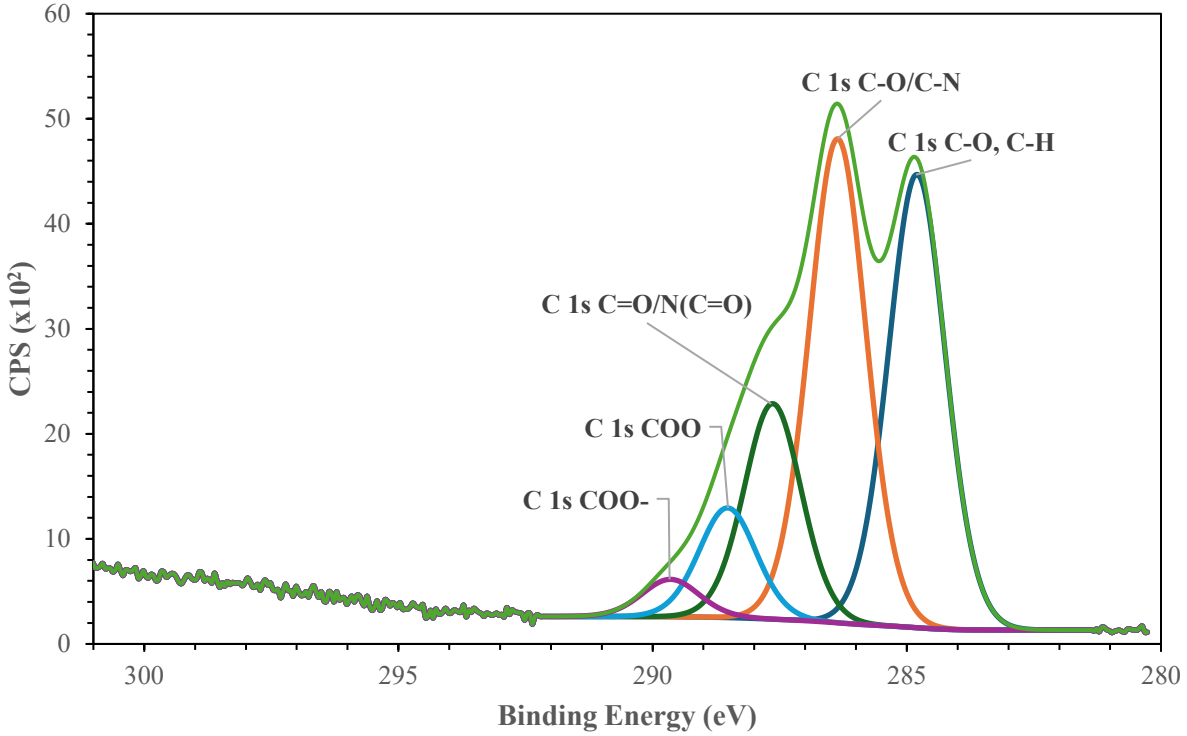

Figure 4.4: XPS spectra of C1s peaks on oxidized fibres.

4.3.1.3 Scanning Electron Microscopy

SEM analysis was performed to visualize the surface morphology of flax fibres before and after pre-treatment and after oxidation. Chemical treatments, in the form of acetone and alkali baths, were implemented to remove wax, hemicellulose, and lignin and to aid in the exposure of cellulose microfibrils embedded within these materials to the fibre surface. Furthermore, oxidation treatment was used to functionalize the surface groups on cellulose exposed by earlier treatments.

SEM imaging was conducted on three samples of fibres, each at a different step in the modification process: non-treated, pre-treated, and oxidized. Sample preparation began with the chemical pre-treatment of a single batch of fibres. Once pre-treated, the fibres were then oxidized with the TEMPO radical following the procedure outlined in this research. From this batch, a small amount of fibre was separated before chemical pre-treatment (as the non-treated control), and another small amount was separated after chemical pre-treatment (before oxidation) as the pre-treated sample. All three samples were dried in an oven at 50 ºC overnight and placed in sealed containers until SEM was conducted.

When comparing the images of each sample, there is a clear distinction between the fibres as received compared to those after chemical pre-treatments, with minor differences being noted between the pre-treated and oxidized samples. Figure 4.5 shows a textured and irregular surface for the non-treated fibres. Extractives can also be observed on the fibres, in the form of waxes and proteins that will be removed during the pre-treatment process. When comparing the images of the non-treated fibres to those of the chemically pre-treated fibres, there is a noticeable difference in surface morphology. Treated fibres, as shown in Figure 4.6, display a more even surface with fewer extractives present. The fibres' surface is observed as visually less irregular, and the fibres are more orderly, suggesting the successful removal of non-cellulosic material by the chemical pre-treatments. Additionally, there seems to be an improvement in the separation between fibres. With the oxidized fibres, there is less of a discernible difference from those that were only chemically pre-treated. Oxidized fibres show similar changes to the surface morphology relative to non-treated fibres; however, determining the efficiency of functionalization is a difficult task. As a result, it is necessary to use results from other characterization techniques, like FTIR and XPS, which are more appropriate for characterizing the impact of TEMPO oxidation on the surface of the fibres, as discussed in the previous sections. It can be concluded, however, that SEM results agree with the previous techniques, showing the chemical treatments are clearly providing effective changes to the surface morphology of the fibres.

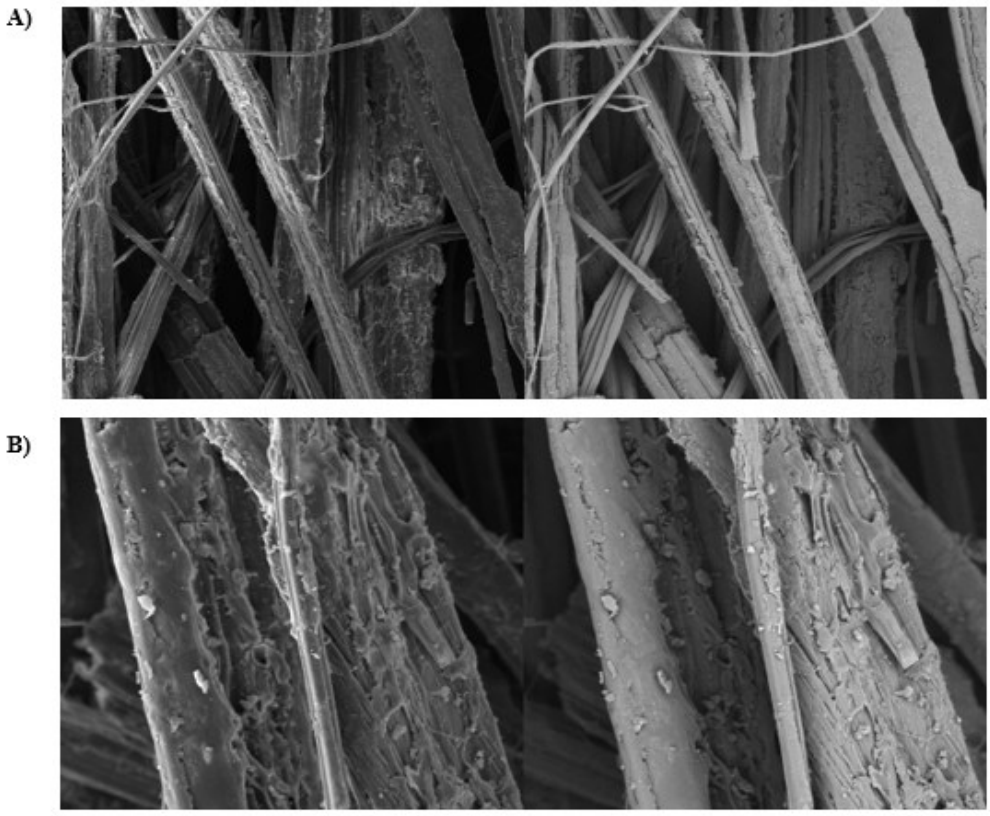

Figure 4.5: SEM images of fibres before any treatment or oxidation, at A) 300x and B) 2000x magnification.

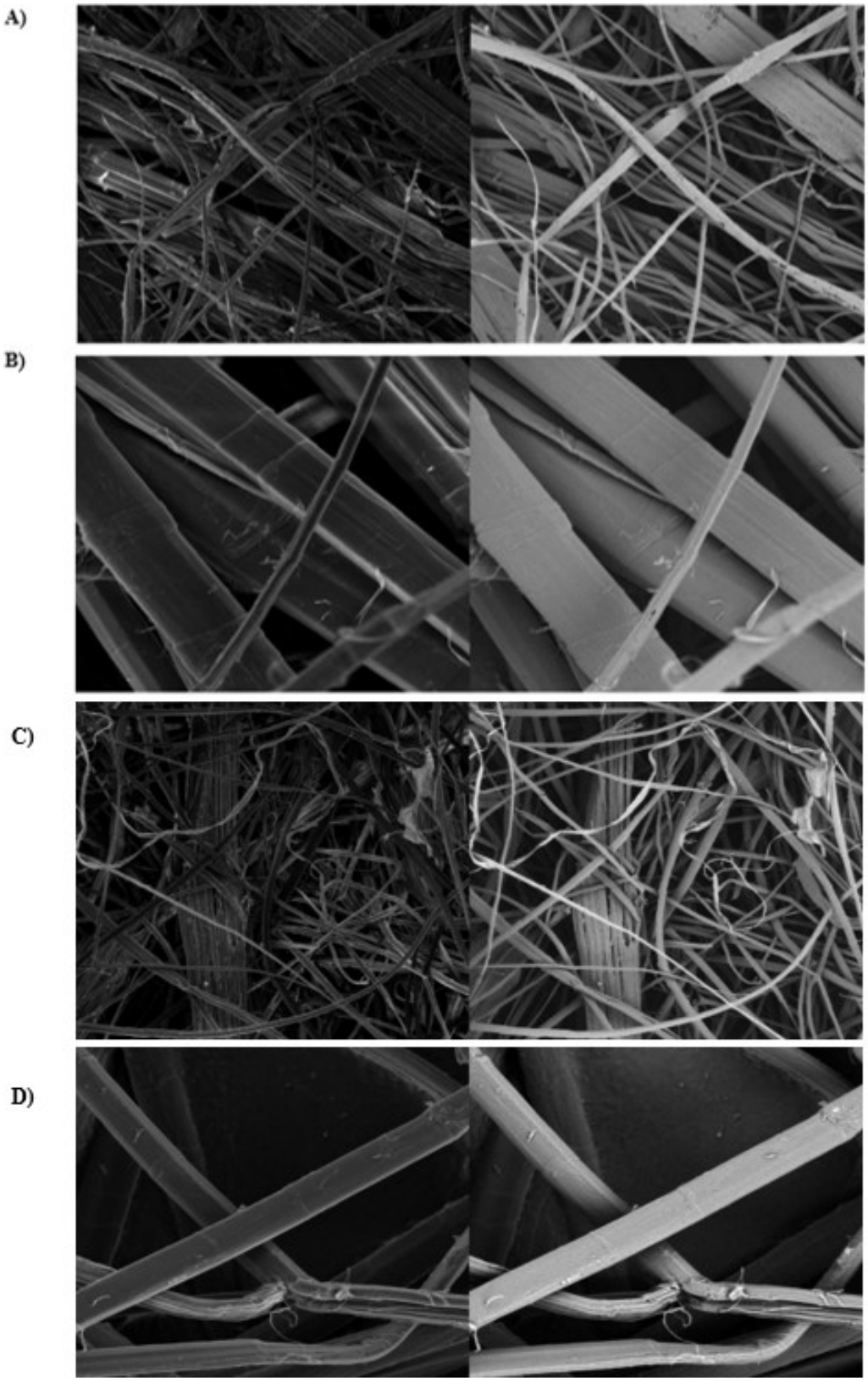

Figure 4.6: SEM images of fibres after treatment, before oxidation, at A) 300x and B) 2000x magnification. Fibres after both treatment and oxidation, at C) 300x and D) 2000x magnification.

4.3.2 Kinetics

Preliminary kinetic experiments were performed to establish the time required for the fibres to reach equilibrium. A maximum time of 24 h was chosen to ensure that fibres were given adequate time to reach equilibrium, and each time interval was tested with 3 replicate samples. The TAN uptake of samples quickly increased within a short period and plateaued after approximately 1 h of contact time (Figure 4.7). The adsorption capacity of samples tested beyond 1 h showed similar, stagnant results in their removal capacity, indicating the equilibrium concentration was achieved.

Two common adsorption kinetic models were applied to further investigate the kinetics of TAN removal using flax fibres. Using linear regression, the best fit among the two models was determined. Results showed the pseudo-second order model provided the best fit, with an R^2 value of 0.999 and a lower RMSE value of 0.043 compared to 0.273 and 0.771 for the pseudo-first order model, respectively. The rate constant for the second order model ($k_2 = 0.179$) was determined using the intercept of the linearized equation plotting t/q_t versus t. The rate constant is then used to determine the q_t values based on the pseudo-second order model, and these values are also included in Figure 7 for comparison to the experimental data. Further evidence to support this model as the best fit was that the calculated value of q_e from the pseudo-second order model matched closely to the experimental data: 1.09 mg/g vs. 1.10 mg/g. These results suggest that chemisorption or ion exchange is the dominant mechanism for TAN adsorption (Khandaker et *al.*, 2021). A fit to the pseudo-second order model denotes that the surface reaction might be the rate-limiting step, i.e., adsorption in which chemical bonding between the adsorbate and functional groups on the surface of the adsorbent establishes the capacity of the adsorbent (Kabir et *al*., 2022; Babakhani and Sartaj, 2022; Halim et *al*., 2010). The model also implies the rate of adsorption is related to the number of available attachment sites, or available functional groups. Thus, as adsorption sites become occupied by the adsorbate, the rate of uptake will decrease and eventually plateau (Kannan et *al.,* 2021; Ebelegi et *al.,* 2020).

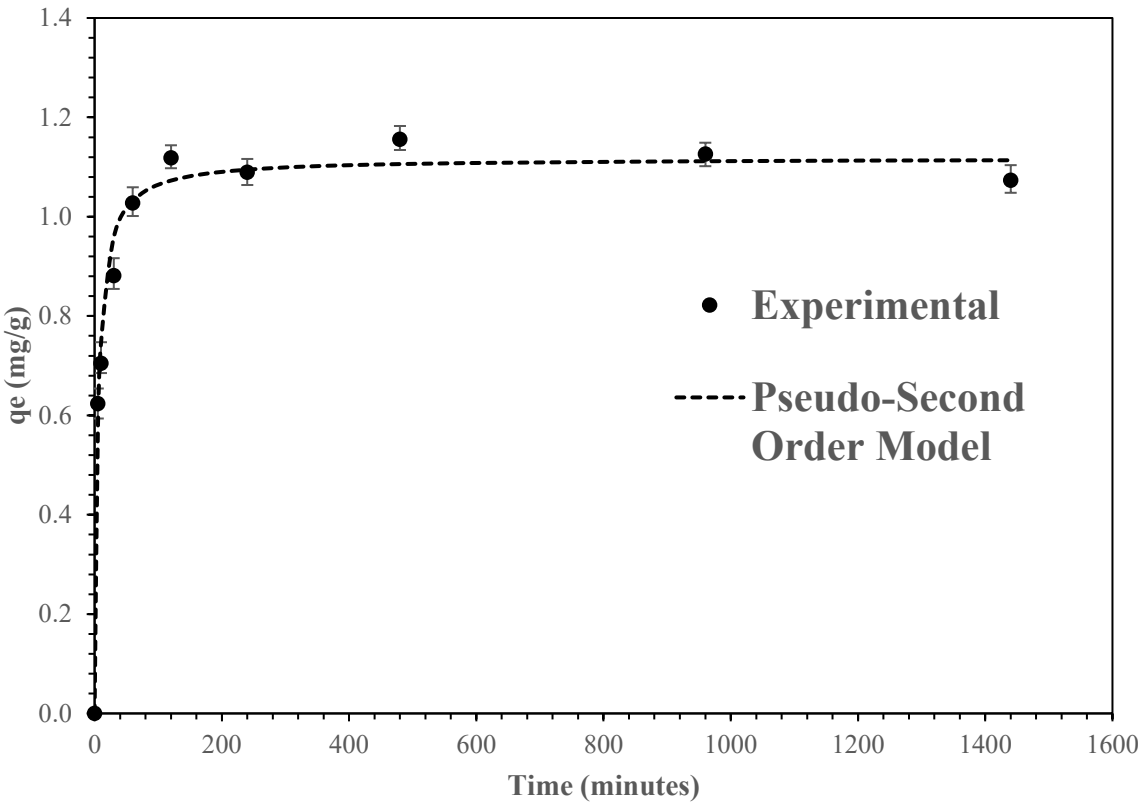

Figure 4.7: Results of kinetic study, as adsorption uptake versus time (Conditions: neutral pH, room temperature; Based on the average of 3 replicates).

4.3.3 Ion Exchange Isotherms

The adsorption uptake for fibres at different phases of the pre-treatment and oxidation process was determined as a function of TAN concentration at equilibrium. TAN uptake was determined using the mass balance of batch tests, with the initial and final concentrations being measured via the Nessler method or with HACH ammonia vials. In this study, Langmuir and Freundlich isotherm models were chosen to investigate the connection linking the fibres' adsorption capacity and the equilibrium concentration of contaminants after testing. Figure 4.8 shows Freundlich and Langmuir fits as well as the experimental data for oxidized fibres. Langmuir isotherm plots for the different levels of modification tested, being non-treated, pre-treated, and oxidized fibres, are shown in Figure 4.9. Using a non-linear regression process in Excel, the experimental data was used to fit to the two models based on initial estimations of the isotherm constants. Results of the non-linear regression were then used to determine the R^2 and RMSE values based on the q_e values generated by the Langmuir and Freundlich equations.

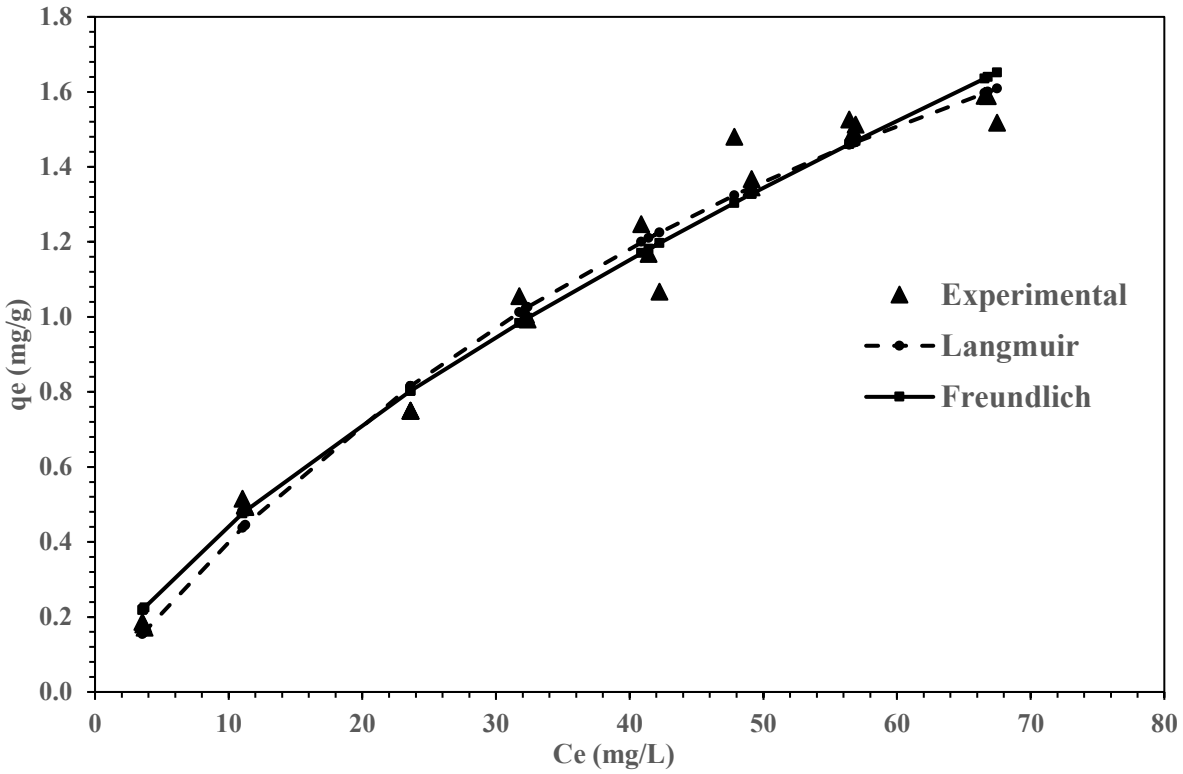

Figure 4.8: Experimental data and adsorption isotherm models of TAN on oxidized flax fibres.

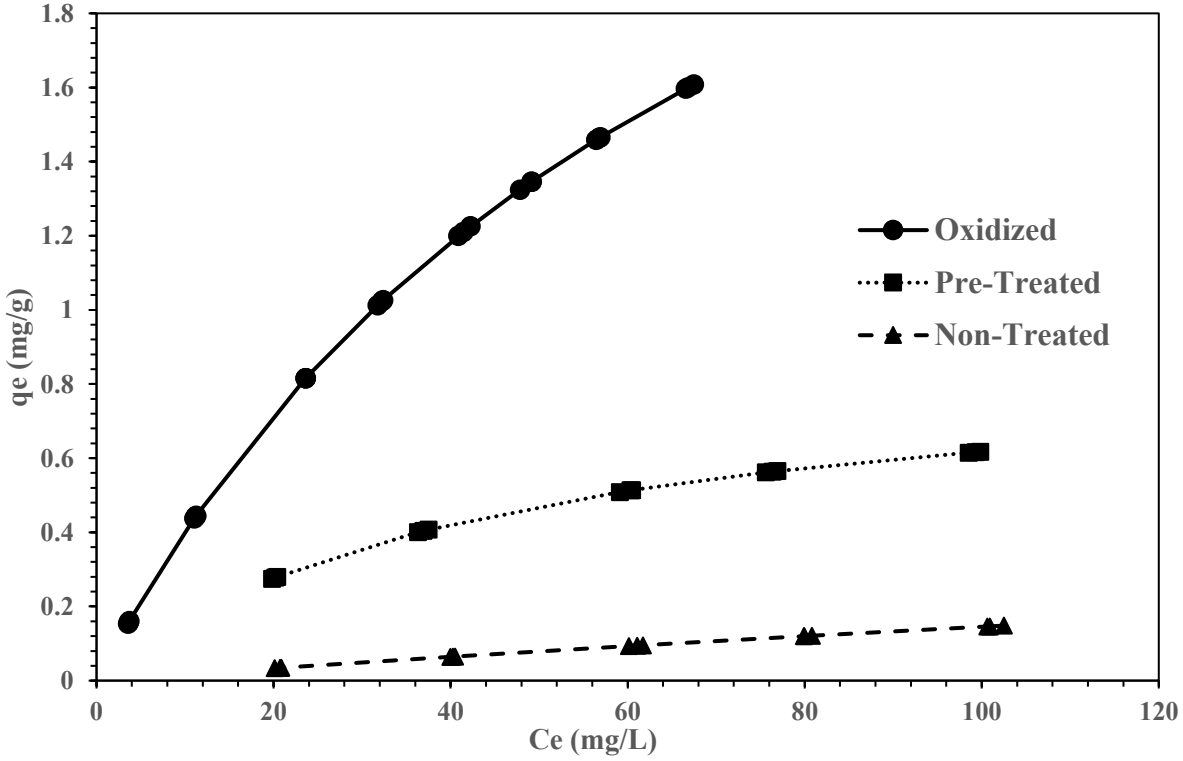

Figure 4.9: Langmuir isotherm plots for the adsorption of TAN on non-treated, pre-treated, and oxidized fibres.

Table 4.2 shows both models performed well in illustrating the adsorption parameters, with coefficient of determination (R^2) values for oxidized fibres of 0.981 and 0.980 for Langmuir and Freundlich, respectively. It can also be noted that the quality of the fit for both models was better for the fibres after undergoing pre-treatment and oxidation versus as received, likely because of the more varied surface characteristics of the non-treated flax. This resulted in the non-treated fibres having more erratic adsorption capabilities within the same batch due to surface extractives like lignin and hemicellulose remaining on the fibres, as compared to chemically treated or oxidized fibres. It was also observed during the testing process that, with the non-treated fibres, extractives leached into the TAN solution, causing a cloudy-yellow colour, which was accounted for when measuring the equilibrium TAN concentration via spectrophotometry. This phenomenon was not observed during the testing of the pre-treated or oxidized fibres, indicating the release of these surface extractives into solution. In addition to the isotherm parameters, root mean square error (RMSE) values were also calculated for the oxidized fibres. Both Langmuir and Freundlich models provided a strong fit to the experimental data of the oxidized fibres, with similar R^2 and RMSE values for each (Table 2). The Langmuir model, however, exhibited slightly better statistical performance, with a marginally improved R^2 and RMSE over the Freundlich model. Additionally, the Langmuir model provides important insights into the adsorption characteristics of the fibres and can be used to determine several relevant parameters, such as the maximum adsorption capacity. A comparison of the maximum adsorption capacity indicated improvement throughout the functionalization process. From the Langmuir equation, adsorption capacity increased from 0.912 mg/g with fibres as received from the supplier to 1.527 mg/g after pre-treatment and to 3.373 mg/g after oxidation, an overall increase of roughly 270%. The large increase in Q_{max} from the pre-treated fibers to the oxidized fibres was a strong indication that the oxidation process is what provided the greatest improvement for the fibres ability to remove TAN. These results are indicative of an overall improvement in flax fibre adsorption characteristics after functionalization. For the oxidized fibres, the Freundlich model's results suggest there is some level of surface heterogeneity for fibres after modification. Practically, this implies a degree of variation of the adsorption affinity across the surface of the fibres and could be a result of TAN being removed by the fibres at sites other than the high-affinity carboxylate groups. The strong fit for the Langmuir model after oxidation indicates that the oxidation process not only improves the uptake capacity of the fibres but also improves the homogeneity of the fibres surface and the adsorption sites found there. Further comparisons can be made using the Freundlich exponent (1/n), a measure of exchange intensity. Pre-treated fibres and oxidized fibres returned 1/n values of 0.660 and 0.687, respectively, and fell in the range of 0.1 – 1, which

suggests TAN removal under favourable conditions. Non-treated fibres, however, resulted in a 1/n value of 1.330, which is outside the range of favourability and aligns with the other indications of poor adsorption properties of the fibres before functionalization.

Table 4.2: Langmuir and Freundlich isotherm constants for TAN adsorption on fibres.

Isotherm Constants	**Condition of Fibres**		
	Non-treated	**Pre-treated**	**Oxidized**
Langmuir			
q_{max} (mg/g)	0.912	1.527	3.373
b (L/mg)	0.002	0.008	0.013
R^2	0.493	0.925	0.981
RMSE	-	-	0.064
Freundlich			
K_F (L/mg)	~0.000	0.034	0.092
1/n	1.330	0.660	0.687
R^2	0.651	0.955	0.980
RMSE	-	-	0.067

The adsorption performance of flax fibres compared with several other biosorbents as well as traditional media is summarized in Table 4.3. Although conventional materials such as zeolites and synthetic resins typically exhibit higher adsorption capacities than flax fibres, results fall within or greater than reported values for most organic adsorbents. It should be noted that uptake capacity values can fluctuate between media based on differences in contaminant concentration and initial adsorbent dose, and as such, test conditions have also been listed in Table 4.3. However, notable qualities of flax fibres include a strong rate of adsorption relative to other biosorbent materials and low cost. In the case of cellulose-based adsorbents, theoretically, the ability to remove TAN is determined by the number of carboxylate groups accessible on the fibre surface, and therefore, the improvement of the oxidation process could be one method to yield improved uptake values.

Table 4.3: TAN adsorption capacities of various natural and synthetic adsorption media.

Material	q_{max} (mg/g)	Contact Time to Equilibrium (hours)	Initial Conditions (Temperature, Ammonia Concentration, pH)	Dose Size (g/L)	Reference
Flax Fibres	3.37	1	24°C, 10 – 100 mg/L, 7±0.5	10	This study
***P. Oceanica* Fibres**	2.11	0.5	30°C, 10-50 mg/L, 6	3	(Wahab et *al.*, 2010)
Modified Rice Straw	2.60	1	24°C, 3 – 25 mg/L, 7.5±0.5	2	(Khalil et *al*, 2018)
Cactus Leaves Fibres	2.58	0.5	30°C, 10-50 mg/L, 7	5	(Wahab et *al.*, 2012)
Clinoptilolite	2.80	0.5	22°C, 10-70 mg/L, 7.9±0.4	100	(Sheikh et *al.,* 2023)
Natural Zeolite	13.2	4	26.1°C, 36 mg/L, 6.8±0.2	5-30	(Wang et *al.*, 2015)
Dowex Synthetic Resin	1.81	0.33	22.5°C, 3.8-22.7 mg/L, 7	12.5	(Al-Sheikh et *al.,* 2020)
Amberlite ion-exchange resin	29.80	0.5-1	26°C, 300-3000 mg/L, 6 – 9.2	25	(Ding and Sartaj, 2016)

4.3.4 Effects of Temperature Change and Thermodynamic Analysis

The impacts of temperature differences on the adsorption mechanism of oxidized fibres were studied by performing batch testing in a simulated low-temperature environment. A set of batch adsorption tests was conducted at 4 °C with the remaining preparation and parameters following the batch testing procedure outlined previously. Results shown in Table 4.4 indicate that adsorption capacity decreased slightly with a drop in temperature, with Q_{max} at 4 °C of 2.272 mg/g compared to 3.373 mg/g at 23 °C.

Table 4.4: Langmuir and Freundlich isotherm constants and R^2 values for TAN adsorption on fibres at two temps.

Isotherm Constants	Temperature	
	23 °C	**4 °C**
Langmuir		
q_{max} (mg/g)	3.373	2.272
b (L/mg)	0.013	0.012
R^2	0.981	0.994
Freundlich		
K_F (L/mg)	0.092	0.053
1/n	0.687	0.734
R^2	0.980	0.981

An improvement in removal percentage and adsorption capacity with increased temperature would indicate the process is endothermic, and this can be further determined with a thermodynamic analysis (Nandi et *al.,* 2009). Thermodynamic properties of the adsorption process can be determined using the following equations (Liu, 2009; Milonjic, 2009):

$$\Delta G = -RTln(\frac{K_L \cdot q_{max}}{1 + K_L \cdot q_{max}}) \quad \text{(eq. 4.7)}$$

$$\Delta H = R \frac{\ln(\frac{K_{L2}}{K_{L1}})}{(\frac{1}{T_1} - \frac{1}{T_2})} \quad \text{(eq. 4.8)}$$

$$\Delta S = \frac{\Delta H - \Delta G_{1,2}}{T_{1,2}} \quad \text{(eq.4.9)}$$

Where ΔG is Gibbs free energy (J/mol), ΔH is enthalpy change (J/mol), ΔS is entropy change (J/mol. K), and R is the universal gas constant (8.314 J/mol. K), K_L is the Langmuir constant at a given temperature, Q_{max} is the maximum adsorption capacity at a given temperature, and T is temperature measured in Kelvin.

Results from the Langmuir models of each isotherm were used for the calculation of the Gibbs free energy with the Van't Hoff equation. In the case of neutral or weakly charged adsorbents, such as $NH4^+$, the Langmuir constant can be considered numerically equal to the thermodynamic equilibrium constant used in these calculations. This is because the ionic strength of the solute, a parameter used in determining the thermodynamic equilibrium constant, is assumed to be negligible due to the weak charge of the contaminant species. Therefore, it can be used as an approximation of the equilibrium concentration (Liu, 2009). Data from the model can all be applied to a rearranged form of the equation to calculate the enthalpy change. Finally, entropy change can be determined using the values calculated based on the Gibbs free energy and enthalpy change. These parameters are summarized in Table 4.5.

Table 4.5: Thermodynamic parameters of TAN adsorption onto oxidized flax fibres.

Temperature (K)	**ΔG (J/mol)**	**ΔH (J/mol)**	**ΔS (J/mol. K)**
296.15	7,805	2,874	- 16.64
277.15	8,936	2,874	- 21.87

A positive value of enthalpy change confirms the endothermic nature of the process, in agreement with the experimental data. This also suggests fibres require some level of energy input from their surroundings to help facilitate the adsorption process. A positive ΔH value additionally suggests that the chemisorption mechanism is controlling the adsorption of TAN (Hossain et *al*., 2022). Furthermore, a negative value of entropy change is indicative of increasing order in the system during adsorption. More specifically, the disorder in the system is reduced such that adsorbed molecules will become more constrained in the positions of the surface of the adsorbate. A positive value of Gibbs free energy is an indication that the adsorption process is non-spontaneous at the given conditions and therefore not necessarily thermodynamically favourable (Basu et *al.*, 2019). Although, according to Gibbs free energy, the process is non-spontaneous at the current conditions, there are several factors that drive adsorption. The high affinity of the specific functional groups and adsorption sites (in this case, the carboxylate groups) can allow for the adsorption of TAN and overcome the non-spontaneity of the reaction. The process may also be kinetically favourable and establish a rate of adsorption that can achieve increased removal (Ebelegi et *al.,* 2020; Weng et *al.,* 2007). Given these results, it is likely that the process is not thermodynamically favored under the conditions tested, but there are still other significant factors that drive the adsorption process and drive the removal of TAN. Additionally, results indicate that uptake could be increased by operating the system at higher temperatures, which may increase the thermodynamic favourability of the process.

4.3.5 Effects of pH Change

A batch test was also conducted to determine the effect of pH on the removal of TAN from solution. Multiple samples were tested in various solutions at room temperature with differing pH values ranging from 4 to 9. The resulting uptake for each of the tested pH values ± the standard deviation is shown in Figure 4.10. The data shows that exchange capacity increases slowly and reaches its peak at a pH of 6.5. The values then continue to decrease after the peak.

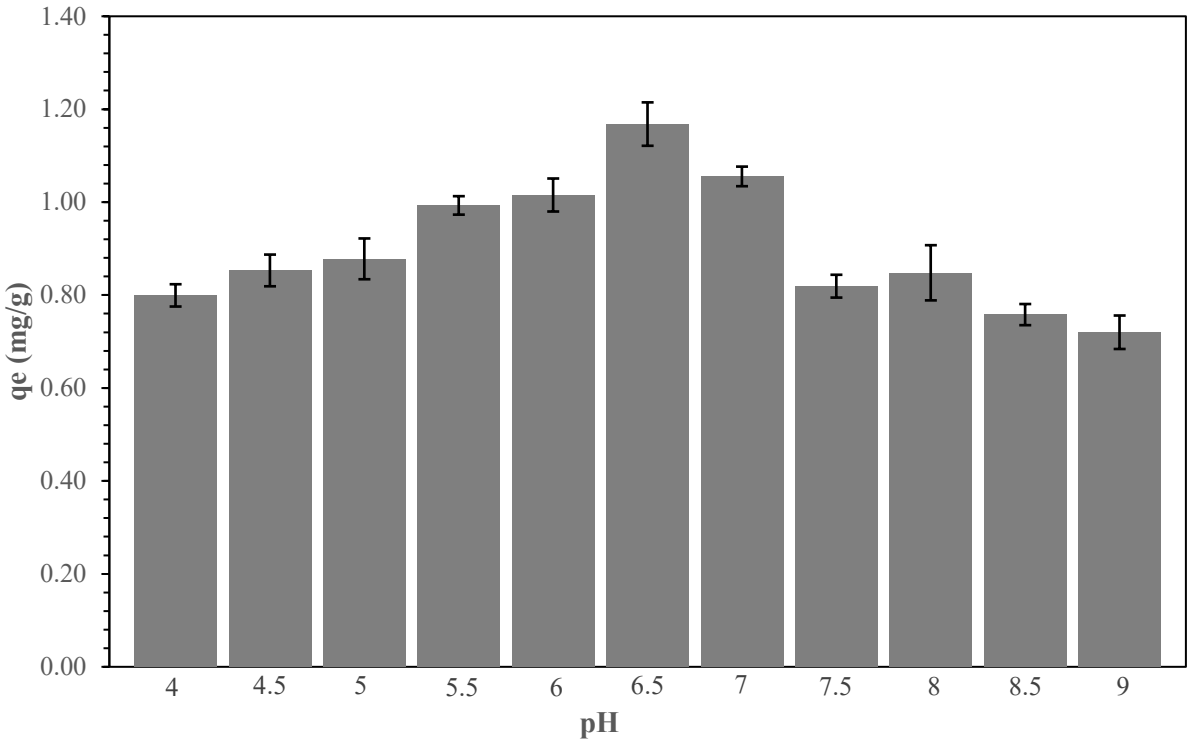

Figure 4.10: Effect of pH on the adsorption capacity of flax fibres (initial TAN concentration of 40 mg/L and adsorbent dose of 0.5g).

These differences in exchange capacity may be a result of the fluctuations in ionized and unionized ammonia as the pH of a solution changes. At a pH value of 9 or lower, ionized ammonia (NH_4^+) is present in higher concentrations relative to the unionized form (NH_3) and reaches almost 100% at a pH value of 7. Relating to the removal of TAN via ion exchange, it is preferred in almost all cases to have ammonia remain in its ionized form, as the charge of the species is a driving factor for removal through adsorption or ion exchange. An analysis of variance (ANOVA) was done to establish any statistical significance between the pH levels. With a significance level of 0.05, the much smaller p value, determined to be ~0.0002, indicates a statistical significance in the uptake capacities across the different pH values. Based on the distribution of the two species at various pH levels, a very mildly acidic or neutral pH solution would be ideal for optimal removal conditions. Results also suggested that trending too far below a pH of 7 could also be slightly detrimental to the removal efficiency. Although under acidic conditions ammonia will be present as NH_4^+, there is also an increase in the concentration of H^+ ions, which has the possibility of creating competition for the exchange sites on the surface of the fibres (Xue et *al.,* 2019; Huang et *al.,* 2010).

3.6. Regeneration

Regeneration tests were also conducted as a means of a) determining the extended performance of the fibres through regeneration cycles and b) determining the effects of different regenerant solutions. Regeneration experiments were conducted only on fully treated and oxidized fibres, which were prepared following previously outlined procedures. A total of three loading and regeneration cycles were performed, with analysis done after each cycle to allow for a comparison of efficiency at each step. Figure 4.11 shows the average adsorption capacities ± standard deviation of replicated samples of oxidized fibres throughout the various loading cycles for the different regenerate solutions.

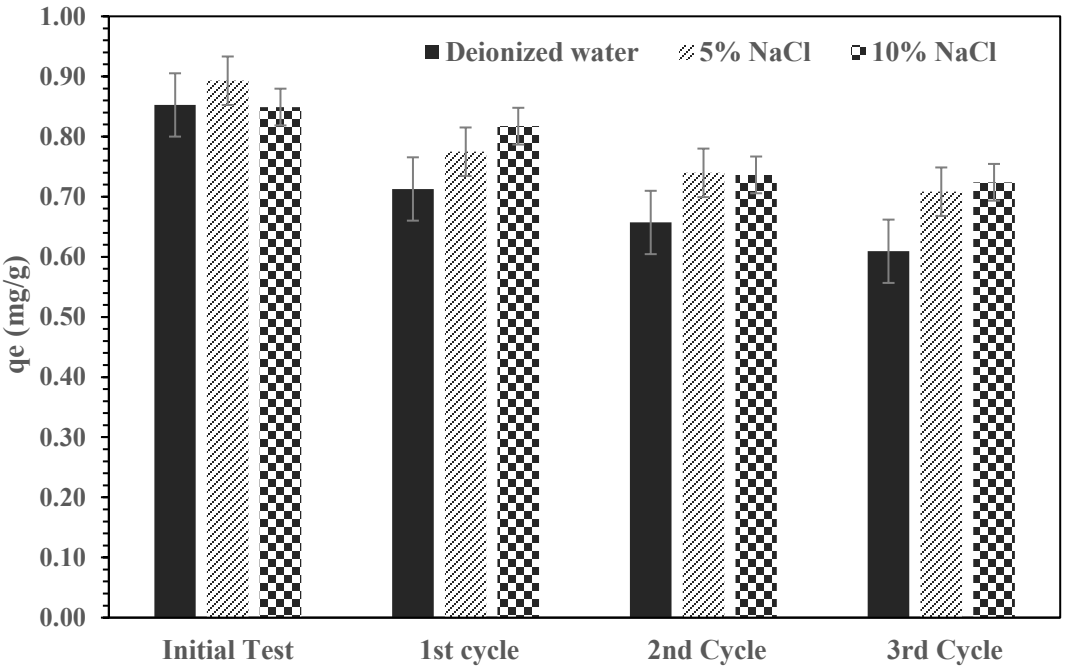

Figure 4.11: Average TAN exchange capacity of flax fibres through 3 regeneration cycles using various regeneration solutions (Conditions: C_0 = 35 mg/L, dose size = 0.5g, room temperature).

The results of the regeneration tests indicated a slight drop in uptake throughout the loading and unloading cycles. Of the three regenerant solutions used, 10% NaCl generated the smallest drop in uptake, with around a 13% decrease after the third cycle when compared to the initial test. Conversely, the simple regeneration procedure of deionized water proved to produce the largest decrease in contaminant uptake. Although uptake values did decline, there was still significant regeneration potential that allowed for fibres to be reused for some time. An analysis was also performed to establish the statistical significance of the sodium solutions when compared to regeneration using deionized water. Paired t-test confirmed a statistically significant improvement in regeneration efficiency for both the

5% and 10% sodium solutions ($p < 0.05$). This indicated that both sodium solutions exhibited a statistical improvement in the regeneration of fibres when compared to deionized water. A comparison of the 5% and 10% solutions, however, returned a p-value of >0.05, meaning no statistical significance between them. The lack of significance implies that the differences in the capacity of fibres after regeneration with the different sodium solutions are not meaningful; thus, both solutions have statistically a similar effect on the regeneration process. As such, it would therefore be more cost-effective to apply the 5% solution for regeneration since fewer chemicals would be required to produce a statistically similar result to the 10% solution.

Potential causes for the decrease in uptake include the loss of some fibre mass during the separation and cleaning process or because of the degradation of fibres during several loading and unloading cycles, leading to the loss of adsorption sites. It is worth noting that an increased regeneration period could also improve the regeneration characteristics of the fibres, as some studies on the regeneration of adsorption materials have indicated that in some cases, 48 h or more of regeneration time is needed for effective desorption (Han et *al.,* 2021).

4.4 Conclusion

Results indicated that there is potential for the flax fibres (an agricultural waste) to be applied as a low-cost alternative biosorbent material for the removal of TAN from aqueous solutions. Uptake capacities were shown to have improved significantly after the treatment and oxidation processes, with a maximum increase of 270% when compared to fibres without any chemical alterations. Adsorption isotherms derived from batch testing results could be well fitted to both the Langmuir and Freundlich isotherm models, with results of modified fibres using the Langmuir model giving an R^2 values of 0.981 and a maximum adsorption capacity of 3.373 mg/g.

Kinetic testing determined equilibrium was reached relatively quickly, at about 1 h of contact time. Additionally, the pseudo-second order kinetic model was a strong fit with the experimental data, implying a dominant adsorption mechanism of chemisorption or ion exchange. pH testing revealed that neutral to very slightly acidic conditions at pH 6-7 created an environment for efficient adsorption due to the distribution of NH_3 and NH_4^+ in this range. Furthermore, thermodynamic analysis indicates that the removal process is endothermic in addition to being favorable and spontaneous. The process was found to also be more favorable with increasing temperature, with slight decreases in uptake capacity in colder conditions versus room temperature. Further analysis was conducted to establish the ability of the fibres to be regenerated and reused for multiple treatment cycles. Slight drops in uptake capacity

were seen after three regeneration cycles for all solutions, with the 10% NaCl solution generating a 13% drop in uptake versus a 30% decrease using deionized water.

Finally, surface characterization provided insight on the surface morphology and chemical bonds present after chemical treatment and oxidation. Surface imaging gave a visual indication of the removal of extractives after chemical treatment of the fibres, showing fewer surface irregularities and more uniform fibres. More detailed analysis of the surface characteristics corroborated the conclusions made from imaging relating to the removal of extractive materials. Additionally, data from FTIR and XPS analysis also gave strong suggestions for successful surface modifications, as many indicators of sodium carboxylate being introduced to the fibres were found.

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Chapter 5: Conclusions and Future Work

5.1 Conclusions

The study investigated the efficacy of flax fibres treated with TEMPO oxidation for the removal of ammonia from aqueous solutions. Flax fibres, an abundant and sustainable material, were chemically treated and then oxidized using the TEMPO radical to enhance their adsorption capacity. Batch adsorption tests revealed a meaningful increase in adsorption capacity after treatment and oxidation. Langmuir isotherms indicate a maximum capacity of 3.373 mg/g, a notable improvement over the non-treated fibre capacity of 0.912 mg/g. Moreover, the process demonstrated favorable kinetics, endothermic behavior, and non-spontaneous adsorption with increased efficiency at higher temperatures and near-neutral pH. Regeneration studies highlighted the potential for repeated use of treated fibres, albeit with a slight decrease in uptake capacity over cycles.

SEM, FTIR, and XPS analyses confirmed successful surface modifications. Notable was the removal of non-cellulosic matter from the fibres surface, seen in both SEM imaging and in the lack of bonds indicating the presence of these materials. Additional observations made from FTIR and XPS analysis was the introduction of carboxylate groups, indicative of successful TEMPO oxidation.

In conclusion, the research underscores the viability of flax fibres subjected to TEMPO oxidation as an environmentally friendly alternative material for TAN removal. The findings contribute to the growing body of knowledge on sustainable wastewater treatment methods, highlighting the potential of utilizing agricultural waste products in pollution mitigation efforts. Further optimization and scalability of the process could lead to practical applications in industries facing TAN contamination, advancing both environmental protection and resource utilization objectives.

5.2 Recommendations for Future Work

- Considering only batch loading experiments were performed, column studies could be conducted by packing treated flax fibres into a small-scale column for continuous flow testing.
- Studies could be conducted using real wastewater samples to determine the effects of other contaminant species being present and how that may impact the selectivity and uptake capacity of TAN.

- Several studies have been conducted using microcrystalline cellulose or other mechanically broken-down cellulosic materials with the goal of increasing surface area for better removal efficiency. Therefore, there is potential for research to be conducted using flax fibres mechanically fragmented from their fibrous state.
- Regeneration work can be conducted with further loading and regeneration cycles to determine the efficiency of significantly longer-term use.
- Other methods of oxidation could also be evaluated for comparison relative to TEMPO. Additionally, there is an opportunity to study combinations of treatment and oxidation processes to improve the effectiveness of these modifications.