Rheology and dye adsorption of surfactant-cellulose nanocrystal complexes

by

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Abstract

The adaptability of Cellulose Nanocrystal (CNC) with reference to two of its major applications, namely viscosity modification in complex fluids and dye adsorption, is investigated. In the context of viscosity enhancement, the interaction of CNCs with two ionic surfactants, namely sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB), has been explored in this study. The effect of CTAB and SDS on surface charge of CNCs is analyzed and coupled with the rheological properties in order to investigate the mechanisms in CNC/surfactant and CNC/CNC interactions. It was found that both surfactants result in gelation of chiral nematic CNC suspensions by setting the stage for establishment of crosslinks between individual CNCs. In the case of CTAB, a gradual increase in the viscoelastic moduli was observed with the concentration of surfactant implying the induction of dominant attractive forces between CNCs by surfactant molecules. However, the presence of SDS results in the emergence of both attractive and repulsive forces whose dominance controls the viscoelastic properties.

In the context of dye adsorption, a CNC based adsorbent was first synthesized by modifying the pristine CNC with various amounts of CTAB and consequently was used to study the adsorption behavior of Congo red (CR) in aqueous medium. The interaction of CTAB with CNC, and potential alterations on the chemical and physical structure of CNC was studied. The synthesized adsorbent, a modified cellulose nanocrystal (MCNC), was characterized using Fourier transform infrared (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and zeta potential analysis. The amount of surfactant used for modification exhibited an optimum at which the adsorption capacity was shown a weak maximum. Furthermore, it was found that the amount of surfactant affects the CR-MCNC interactions and determines the mechanisms of
adsorption. Characterization of the adsorbent, before and after adsorption, coupled with kinetics and isotherm studies implied electrostatic attraction, hydrogen bonding, and hydrophobic attraction as the main mechanisms of adsorption. Thermodynamic studies on the system suggested that the adsorption process is spontaneous and exothermic. Finally, stability analysis in aqueous environment revealed that the adsorbent is highly stable and retains its original adsorption capacity after successive dialysis cycles.
Lay Summary

Cellulosic materials have always been in the center of attention for scientific and commercial applications due to their renewability, abundance and versatility. Cellulose nanocrystal (CNC) is a cellulose-based nanomaterial which is produced by chemical treatment of native cellulose. In addition to the innate properties of cellulose, CNCs exhibit some unique features, including high mechanical strength, great functionalization capacity and high surface area, which have promoted them for a wide variety of applications in biological and industrial fields. This study focuses on investigating the adaptability of CNC to two of its most prominent applications, rheology modification of complex fluids and dye adsorption. Due to the typical presence of surfactants in complex fluids, the interaction of CNCs with two ionic surfactants are studied within CNC suspension. In addition, the effect of a cationic surfactant is explored on the anionic dye adsorption properties of CNCs.
Preface

This research was conducted under the supervision of professor Savvas G. Hatzikiriakos in the Chemical and Biological Engineering department at the University of British Columbia. I was responsible for conducting literature review, identifying the knowledge gap, constructing and evaluating hypotheses, defining objectives, designing experimental protocols, performing experiments, and compiling and interpreting results.

Two journal papers are prepared and ready for submission based on the results in chapters 5 and 6 of this thesis. The formulation of the paper, based on chapter 6, was implemented in conjunction with Dr. MacLachlan, Milad Raeiszadeh Oskouei and Lev Lewis who are acknowledged for their contributions and are included as co-authors in the associated paper.

Rheological experiments were conducted in Rheology Lab in conjunction with Dr. Hatzikiriakos. SEM imaging was conducted in UBC Bioimaging Facility.
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List of Symbols

G’  Storage modulus (Pa)
G”  Loss modulus (Pa)
G*  Complex modulus (Pa)
η    Viscosity (Pa.s)
ω    Angular frequency (rad/s)
γ̇   Shear rate (s⁻¹)
C    Concentration (mg/L)
q    Adsorption capacity (mg/g)
V    Volume (L)
t    Time (s)
K₁   Rate constant of pseudo-first order kinetic model (min⁻¹)
K₂   Rate constant of pseudo-second order kinetic model (g.mg⁻¹.min⁻¹)
Kᵢ   Rate constant of intra-particle diffusion kinetic model (mg.g⁻¹.min⁻⁰.⁵)
Kᴸ   Langmuir constant (L/mg)
Kₚ   Freundlich constant (L/mg)
R²   Correlation coefficient
G    Gibbs free energy (kJ/mol)
H    Enthalpy (kJ/mol)
S    Entropy (J K⁻¹ mol⁻¹)
T    Temperature (K)
R    Ideal gas constant (J mol⁻¹ K⁻¹)
## List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force microscopy</td>
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<tr>
<td>CMC</td>
<td>Critical micelle concentration</td>
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<tr>
<td>CNC</td>
<td>Cellulose nanocrystal</td>
</tr>
<tr>
<td>CTAB</td>
<td>CetylTrimethylAmmonium Bromide</td>
</tr>
<tr>
<td>DI</td>
<td>De-ionized</td>
</tr>
<tr>
<td>DLS</td>
<td>Dynamic light scattering</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>ITC</td>
<td>Isothermal titration calorimetry</td>
</tr>
<tr>
<td>MCNC</td>
<td>Modified cellulose nanocrystal</td>
</tr>
<tr>
<td>SDS</td>
<td>Sodium Dodecyl Sulfate</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>TTAB</td>
<td>Tetradecyl Trimethyl Ammonium Bromide</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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## Glossary

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
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<tbody>
<tr>
<td>Admicelle</td>
<td>Aggregates of surfactant molecules attached to the surface of a particle</td>
</tr>
<tr>
<td>CMC</td>
<td>The concentration above which surfactant molecules form micelles</td>
</tr>
<tr>
<td>Micelle</td>
<td>Aggregates of surfactant molecules</td>
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And finally, I would like to express my deepest appreciation and gratitude to my lovely parents, Dr. Mohammadbagher Ranjbar and Naghmeh, grandparents, Fereshteh and Tataneh, my wonderful sister, Dina, and my lovely Sara.
Dedication

Dedicated to my parents, grandparents, sister, love

And

My passed away grandmother, Mahpari

May your soul rest in peace
Chapter 1: Introduction

Cellulose is the main structural component of green plants and is deemed to be the most abundant and renewable source of organic compounds on Earth. Abundance, versatility, biodegradability, and environmental friendliness are some of the main features that have promoted cellulosic materials for a wide variety of applications in sustainability, pulp and paper, construction, manufacturing, and food industries [1]–[3]. In the native cellulose fiber, the cellulose chains form an interconnected network due to the intermolecular hydrogen bonds resulting in the formation of substructures called microfibrils [4]. These microfibrils are composed of crystalline and amorphous regions with crystalline regions having higher density, aspect ratio, and surface area compared to the amorphous ones [5]. These features have drawn interest into extracting the crystalline parts from the cellulose fibers and adapting them to miscellaneous applications.

Various chemical, mechanical, and enzymatic treatments have been employed to release the highly crystalline parts of microfibrils among which sulfuric acid hydrolysis has been particularly interesting as it releases the crystalline parts in the form of crystallites referred to as cellulose nanocrystals (CNC) [6]. The CNCs that are produced through acid hydrolysis exhibit unique features including high surface area and aspect ratio, hydrophilicity, broad functionalization capacity, chirality, and mechanical strength. Furthermore, the presence of sulfate ester groups results in a high negative charge density on the surface of CNCs, which make them dispersible in aqueous medium. These exceptional characteristics have promoted CNCs for a wide range of applications including tissue engineering [5], drug delivery [7], dye adsorption [8], and rheology modification of complex fluids [9].
Mechanical strength and stiffness are two of the main factors that have made CNCs suitable as reinforcement elements in composite materials [10]. Furthermore, the high shear sensitivity of CNC suspensions over a wide range of concentrations have drawn interest into studying their rheology and their potential in modifying the rheological behavior of other composite materials [4]. The rheology of CNC suspensions, its dependence on CNC concentration, and its relationship with the micro-structure of CNC suspensions have been well evaluated and documented during recent years [11]–[13]. Furthermore, CNCs could result in considerable reinforcements in the structure of polymer matrices [14] and alterations in the rheological behavior of composite hydrogels [15].

In the context of using CNCs as rheology modifiers in complex fluids, one of the most important effect that needs to be rigorously assessed is the interaction of CNCs with surface active agents, namely surfactants, which are usually present in complex fluids. Recently, the effect of surfactants on hydrophilicity, stability and dispersion of CNCs in aqueous medium has been investigated and the physicochemical properties of CNC suspensions have been characterized in the presence of different surfactants [16]–[18]. Nevertheless, to the best of our knowledge, there have been no systematic studies performed on the rheology of CNC suspensions in the presence of surfactants and the potential mechanisms that alter the rheological behavior of CNC suspensions. In the first part of this research, a rigorous investigation was performed on the effect of a positive surfactant, CetylTrimethylAmmonium Bromide (CTAB), and a negative surfactant, Sodium Dodecyl Sulfate (SDS), on viscosity enhancement and gelation of CNC suspensions. Furthermore, the possible mechanisms resulting in the adjustment of viscosity and gel formation have been elucidated by investigating the zeta potential of CNC suspensions and the effect of ionic strength.
As previously discussed, the unique properties of CNCs have promoted them for a wide variety of applications among which the capability of CNCs in adsorbing industrial dyes has been particularly interesting. This is examined and studied in the second part of this research work.

Dyes and pigments are extensively used in industries such as textile, leather, pharmaceutical, food, and cosmetic [19]. The continued discharge of wastewater containing dyes into the environment may give rise to many human health and environmental issues due to their toxicity, potential carcinogenicity, and mutagenicity [20], [21]. High stability and solubility as well as non-biodegradability of industrial dyes have raised the need for adequate and effective treatment of the wastewater before entering the environment [22]. During the past decades, various biological and physicochemical methods have been developed for the treatment of contaminated wastewater, including photocatalysis [23], catalytic degradation [24], chemical oxidation [25], membrane filtration [26], and adsorption. Among these methods, adsorption has been considered as the most beneficial due to its high efficiency, low cost, production of fewer byproducts, and simplicity of operation. Various classes of materials including hydrogels [27], modified clay [28], graphene composites [29], and cellulosic extracts [30] have been developed and examined for the adsorption of industrial dyes from wastewater. Despite great progression in this field, the development of novel dye adsorbents continues in order to overcome the existing limitations such as low adsorption capacity and complexity of synthesis.

As for the cellulosic materials, particularly CNC, the existence of glucopyranose and three hydroxyl groups on each hydroglucose unit has not only provided active sites for the adsorption of dye molecules, but it has also made it feasible for various modifications and functionalization that improves the dye removal properties of cellulose [31]. Therefore, there has been a high interest in investigating the dye adsorption properties of CNCs in recent years. Since the
presence of negative charges on the surface of CNCs facilitates the adsorption of cationic dyes, early studies on the adsorption properties of CNCs were mainly focused on cationic dyes [8]. Moreover, various functionalization methods were used to improve the adsorption capacity of CNCs [31]. However, the unique features of CNCs attracted researchers to employ these nanoparticles in the adsorption process of anionic dyes as well. In several studies, CNCs were incorporated in the structure of a composite material to improve its dye adsorption properties. These composite materials include microgels [32], polymeric ionic liquids [33], and thin-film composite membranes [34]. On the other hand, CNCs were adapted to the adsorption of anionic dyes by functionalization of their surface, such as amino-functionalizing, which could improve their adsorption abilities [35]. Nevertheless, to the best of our knowledge, there have been no additional studies, with the exception of the above mentioned, conducted on the adaptation of CNCs to the adsorption of anionic dyes by functionalization of its surface chemistry. Therefore, further research is required in order to gain a better understanding of the potential use of CNCs as adsorbents of anionic dyes.

Among the potential materials for functionalization purposes, surfactants have always been of great interest due to their hydrophilic-hydrophobic nature which sets the stage for their interaction with a wide variety of molecules and functional groups [22]. Another unique property of surfactants is their ability to form bundles of surface-bound micelles, known as admicelles, on the colloidal particles in aqueous environments which could affect the interparticle interactions and induce distinctive features to the colloidal particles [36], [37]. In the past, surfactants have been used in several studies to improve the adsorption abilities of existing dye adsorbents. These studies include the modification of montmorillonite by several cationic surfactants [38], hectorite with CTAB and octadecylamine (ODA) [39], and the synthesis of organovermiculite-based
adsorbent using CTAB [40]. Nevertheless, there are no investigations performed on the potential contribution of surfactants to the anionic dye adsorption of CNCs.

Recently, the effect of a positive surfactant, CTAB, was investigated on the stability and dispersibility of CNC suspensions [18]. The advantages of using CTAB over other materials for the anionic dye adsorption using CNCs include, its biodegradability by suitable micro-organisms [41], low cost, and wide availability. In this study, the same method of modification is used on CNCs [34]. However, a detailed investigation was performed on surfactant-CNC complexes, and the interactions between modified CNCs (MCNCs). The contribution of CTAB to the anionic dye adsorption ability of MCNC, and the optimum conditions of modification are explored. Furthermore, the adsorption behavior of Congo red onto MCNC, including adsorption kinetics, isotherms, thermodynamics, and adsorption mechanisms are discussed. Finally, the stability of MCNC in aqueous environments and the regeneration of the adsorbent are investigated.
Chapter 2: Literature review

2.1 Cellulose nanocrystal (CNC) basics

Strong acid hydrolysis results in the disintegration of cellulosic fibers by attacking the amorphous regions and releasing them in the form of rod-like crystallites, referred to as CNCs. Sulfuric acid is commonly used for the hydrolysis process as it introduces negative charges to the surface of CNCs by converting the hydroxyl groups on the CNCs to sulfate ester groups which make them dispersible in water and prevents their aggregation and sedimentation thus, yielding a stable suspension [4]. In addition, sulfuric acid hydrolysis introduces some other unique properties to the CNCs including high specific surface area (400 m$^2$/g) and high aspect ratio (20) as reported by CelluForce (Montreal, Quebec, Canada). Hydrochloric acid has also been used for acid hydrolysis of cellulosic fibers, but it results in the formation of neutral CNCs tending to aggregate in aqueous suspensions, thus limiting their applicability [42]. The main source of cellulose used for producing CNC is wood fiber, but they have previously been prepared from other sources including, cotton [43], annual plants [44], tunicates [45], and bacteria [46].

2.2 Applications of CNC

Biodegradability and biocompatibility are two of the main factors making CNCs good candidates for biomedical applications where they are used as carriers in drug delivery and nanofillers in tissue engineering [5], [7]. Due to the formation of chiral nematic liquid crystalline phases in concentrated suspensions, films of CNC are cast on cellulosic surfaces to produce different optical properties. These films are important for applications including security papers, certificates and passports. High mechanical strength is the major property promoting CNCs for a wide variety of applications. An axial modulus in the range of 58-180 GPa and tensile strength of
0.30-22 GPa account for the high interest in CNCs as reinforcing components in composite materials. CNCs are used as reinforcing elements in polymeric matrices, coatings and fillers. Furthermore, high shear sensitivity and microstructure transition with adjustable variables (concentration, ionic strength, pH) is another feature that has drawn interest into CNCs to be used as rheology modifiers.

2.3 Rheology of CNC suspensions

Despite their high potential for a wide range of industrial biological applications, the number of recognized commercial CNC-based products are very limited. Therefore, further research is required on different aspects of CNCs in order to investigate their adaptability to different applications and environments. In order to explore the potential of CNCs as rheology modifiers in complex fluids, different aspects of their rheological properties and the effect of environmental variables on these properties should be studied.

2.3.1 Effect of concentration on rheology and microstructure of CNC suspensions

Unlike other cellulosic extracts, such as cellulose nanofibril and microfibril, CNC suspensions experience different microstructural and rheological transitions with the concentration of CNC. Polarized optical microscopy (POM) along with rheology has been used to investigate microstructural states of CNC suspensions at different concentrations.
The steady-state viscosity of CNC suspensions, Figure 2.1, shows three distinct behaviors as the concentration increases. At low concentrations, CNC suspensions show the behavior of an isotropic sample with a Newtonian plateau at low shear rates, a shear thinning trend at intermediate shear rates and a second plateau at high shear rates. To explore the microstructural changes of isotropic samples under shear, POM micrographs of 1 wt% suspension (Figure 2.2), were taken at shear rates 0.01, 0.1, and 10 s\(^{-1}\). The micrographs were dark and did not show any signs of anisotropic ordered phases.

Figure 2.2: Polarized optical micrographs of 1 wt% CNC suspension under shearing at (a) 0.01 s\(^{-1}\), (b) 0.1 s\(^{-1}\) and (c) 10 s\(^{-1}\) with 50 μm scale (reprinted with permission from Shafiei Sabet 2013)
For samples at higher concentrations, i.e. 3 and 4 wt%, the viscosity profile showed a three-region behavior typical of biphasic chiral nematic liquid crystals. At low shear rates (region I), the suspensions showed a shear thinning trend followed by a plateau at intermediate shear rates and a second shear thinning at high shear rates.

Figure 2.3: Polarized optical micrographs of 4 wt% CNC suspension under shearing at (a) 0.01 s⁻¹, (b) 0.05 s⁻¹, (c) 0.1 s⁻¹, (d) 0.5 s⁻¹, (e) 1 s⁻¹ and (f) 10 s⁻¹ with 50 μm scale (reprinted with permission from Shafiei Sabet 2013)
POM micrographs of 4 wt% suspension (Figure 2.3.a-c), revealed that at low shear rates, chiral nematic domains, represented by fingerprints, are deformed and re-aligned resulting in a decrease of viscosity. At intermediate shear rates, all chiral nematic domains become aligned along the shearing direction (Figures 2.3.d and 2.3.e), where the viscosity reaches a plateau. Finally, at high shear rates, all liquid crystalline domains are broken down and individual nanorods are aligned along the shear direction. Therefore, viscosity shows a second shear thinning behavior and the micrograph shown in Figure 2.3.f, becomes dark, implying that chiral nematic domains are not present within the suspension.

At 7 wt%, the viscosity profile shows a single shear thinning behavior over the whole range of shear rates indicating gelation of CNC suspensions at high concentrations. The micrograph of 7 wt% sample presented in Figure 2.4.a shows the structure of a birefringent gel at the low shear rate of 0.01 s⁻¹. As the shear rate increases, the applied shear breaks the structure of gel and releases the ordered domains which are oriented along the shearing direction. The single shear thinning behavior is attributed to two simultaneous mechanisms, which are breakage of gel structure and deformation of ordered domain (Figure 2.4.b-e). At high shear rates, the breakage of liquid crystalline domains sets the stage for alignment of individual rods with the shearing direction, which could be further confirmed from its darker micrograph (Figure 2.4.f).
2.4 Interaction of CNCs with different electrolytes

In the context of using CNCs as rheology modifiers in complex fluids, the interaction of CNCs with surfactants becomes prominent due to the usual presence of surfactants in complex fluids. Previous studies have investigated the effect of ionic and nonionic surfactants on zeta potential and dispersibility of CNCs in aqueous medium. In one study, the zeta potential of dilute CNC suspension (0.1 wt%) was studied as a function of two ionic surfactant concentration [16].
Figure 2.5: Zeta potential versus the concentration of CTAB and SDS with and without 10 mM NaCl
(reprinted with permission from Prathapan 2016)

Figure 2.5 shows the change in the zeta potential of CNC suspension by the addition of surfactants. The positive surfactant, CTAB, was adsorbed to the surface of CNCs through electrostatic attraction which increased the surface potential of CNCs. Therefore, the absolute values of zeta potential decreased significantly with the concentration of CTAB. With further addition of CTAB, the zeta potential reversed and CNCs became positively charged. The continuous adsorption of CTAB onto CNC was attributed to the fact that pre-adsorbed CTAB increases the hydrophobicity of CNCs resulting in an increasing drive in further adsorption of surfactant molecules. As for the anionic surfactant, SDS, the values of zeta potential remained roughly constant up to the critical micelle concentration (CMC), and then started to increase in their absolute value. It was postulated that despite the existence of repulsive forces between CNCs and the anionic surfactant, SDS molecules are still adsorbed on to the less charged regions on the surface of CNCs through hydrophobic attraction between the carbon tails of SDS and cellulose chains. Thereafter, the negative charge density increases on the surface of CNCs upon
adsorption of SDS molecules leading to larger values of the zeta potential at surfactant concentrations above CMC. The coupling effect of surfactant and ionic strength was also studied in the presence of 10 mM NaCl which did not show any considerable changes. A similar trend was observed in the zeta potential in other studies where the interaction of positive surfactants was investigated with cellulosic model films [47], fibers [48] and CNCs [49].

In a separate study, the effect of electrolytes on zeta potential of very dilute CNC suspensions was investigated. This was coupled with atomic force microscopy (AFM) and dynamic light scattering (DLS) to explore any possible changes in the size of CNCs [17].

Figure 2.6: Zeta potential and particle size of CNC versus the concentration of (a) Na⁺, (b) Ca²⁺ and (c) SDS (reprinted with permission from Zhong 2012)
It was found that the addition of both divalent and monovalent cations screened-off the negative charges in the surface of CNCs leading to a decrease in the absolute values of zeta potential, as shown in Figures 2.6.a and 2.6.b. Accordingly, the particle size increases as a result of CNC aggregation at high ionic strength. As for SDS, absolute values of zeta potential increased due to the previously mentioned reasons which consequently resulted in better dispersion of CNCs and smaller particle sizes (Figure 2.6.c).

To gain additional insight into other aspects of CNC-surfactant complexes, interactions of a positive surfactant, Tetradecyl Trimethyl Ammonium Bromide (TTAB) with CNCs was investigated by isothermal titration calorimetry (ITC) [50]. The enthalpy change of 0.655 g/L CNC suspension was measured after injecting various amounts of TTAB ranging from 0 to 1.2 g/L. The enthalpy change with surfactant concentration showed four different regions, presented in Figure 2.7.

![Figure 2.7: Enthalpy change versus the concentration of TTAB for 0.655 g/L CNC suspension (reprinted with permission from Dhar 2012)](image-url)
In region I, surfactant molecules are adsorbed onto the surface of CNCs through electrostatic attraction between the positive heads of TTAB and negative charges of CNCs. In region II, as the concentration of surfactant increases, the bound surfactant molecules reorganize due to the attraction between carbon tails of CNC suspensions. Further increase in surfactant concentration leads to the formation of micelles on the surface of CNCs in region III. These CNC-bound micelles are called admicelles. The attraction between admicelles on the surface of CNC and the negative charges on its adjacent particle results in the aggregation of CNCs. Afterwards, in region IV, further increase in the concentration of surfactant leads to the formation free micelles in the suspension.

2.5 CNCs for dye adsorption

The abundance of functional groups, including sulfate ester and hydroxyl in CNCs, provide several active adsorption sites and broad functionalization capacity, rendering them good candidates for dye adsorption applications. Since the presence of negative charges on the surface of CNCs facilitates the adsorption of cationic dyes, early studies on the adsorption properties of CNCs were mainly focused on cationic dyes [8]. Moreover, various functionalization methods were used to improve the adsorption capacity of CNCs [31]. However, the unique features of CNCs attracted researchers to employ these nanoparticles in the adsorption process of anionic dyes as well. In several studies, CNCs were incorporated in the structure of a composite material to improve its dye adsorption properties. These composite materials include microgels [32], polymeric ionic liquids [33], and thin-film composite membranes [34]. On the other hand, CNCs were adapted to the adsorption of anionic dyes by functionalization of their surface, such as amino-functionalizing, which could improve their adsorption abilities [35].
Chapter 3: Thesis Objectives and Organization

3.1 Objectives

As a novel nanomaterial with unique properties and considerable advantages over the conventional cellulosic materials, CNC is suitable for a wide diversity of applications. This present research is aimed to investigate the potential and adaptability of CNCs for two impactful applications, namely rheology modification of complex fluids and dye adsorption. In the beginning, the interaction of CNCs with two ionic surfactants (one cationic and one anionic) is thoroughly investigated from the rheological and morphological points of views. Afterwards, these findings are used to explore the effect of the cationic surfactant on the dye adsorption properties of CNCs.

This thesis focuses on attaining the following objectives:

A. Investigate the effect of ionic surfactants on rheology, morphology and physiochemical properties of isotropic and chiral nematic CNC suspensions.

B. Characterize the chemical structure, physiochemical properties and morphology of CNCs after modification with a cationic surfactant (CTAB).

C. Investigate the adsorption behavior of an anionic industrial dye (Congo red) onto CTAB-modified CNC (MCNC), including adsorption kinetics, isotherms, thermodynamics, and adsorption mechanisms.

D. Investigate the recyclability and stability of the synthesized adsorbent (MCNC) in aqueous environment.
3.2 Thesis organization

This thesis is organized as follows. In chapter 1, an introduction is provided on the significance of CNCs in different research fields and their adaptability to various applications. This discussion leads to the basic motivation of this research. Chapter 2 consists of a thorough literature review on previously reported research conducted on the use of CNCs and other similar cellulotic extracts in applications of interest to the present work, namely rheology modification and dye adsorption. The objectives and organization of the thesis are discussed in chapter 3. Chapter 4 describes the materials and methodologies used to prepare and investigate the rheological behavior and the physicochemical properties of CNC-surfactant complexes. Furthermore, the methods used for the characterization of MCNC and investigation of its dye adsorption properties are elaborated in this chapter. Chapter 5 focuses on the effect of ionic surfactants on the rheology, morphology and physiochemical properties of isotropic and chiral nematic CNC suspensions and the mechanisms by which the surfactants affect the rheology of CNC suspensions. In chapter 6, the effect of a cationic surfactant (CTAB) is explored on the physicochemical properties, surface chemistry and crystalline structure of CNCs over a wide range of surfactant concentrations. Moreover, the dye adsorption properties of MCNC including the adsorption kinetics, isotherms, thermodynamics, and adsorption mechanisms. Finally, the recyclability and stability of MCNC in aqueous environment is investigated. Conclusions and significance of this research work are summarized in chapter 7. Recommendations for future work are also presented in chapter 8.
Chapter 4: Experimental

4.1 Materials

Cellulose nanocrystals (CNCs) were purchased from CelluForce Inc. (Montreal, Quebec, Canada) in the form of spray dried sodium salts with sulphur content of 0.89 wt% as reported by the supplier. CetyltrimethylAmmonium bromide (CTAB) was purchased from Sigma-Aldrich with 98% purity. 10% aqueous solution of Sodium Dodecyl Sulfate was purchased from Sigma-Aldrich. Congo Red (CR) dye was purchased from Sigma-Aldrich. All solutions, including the surfactant and dye solutions, and CNC suspensions were prepared using deionized (DI) water.

4.2 Sample preparation

4.2.1 Preparation of pristine and surfactant-added CNC suspensions

CNC suspensions with various concentrations (0.1 to 7 wt%) were prepared by dispersing varying amounts of CNC powder, depending on the desired weight percent, in DI water. The suspensions were stirred for 5 h inside a 200 mL beaker before proceeding to the next stage.

Surfactant stock solutions of 5wt% were prepared to be used throughout the experiments. As for the preparation of the CTAB solution, 5 g of CTAB powder was added progressively to a 100 mL beaker containing 95 g of DI water which was being stirred on a hotplate inside a 50°C bath. The stirring continued for roughly 30 min until the CTAB powder was fully dissolved and the solution stabilized. 5wt% SDS solution was prepared by diluting the 10wt% reference solution.

Samples were prepared by introducing 15 mL of CNC suspension into a 100 mL beaker. Appropriate amounts of surfactant were added to the beaker, while being stirred at 500 rpm, to obtain the desired surfactant concentrations (0.2 to 10mM). The stirring continued for 2 h
followed by 1 min of centrifugation at 1000 rpm to remove bubbles. The samples were stored for 12 h before any further characterization to ascertain that the samples have adequately recovered from any disturbances in their microstructure resulting from the shear applied to the suspensions.

4.2.2 Preparation of modified CNC (MCNC) powder

CNC suspensions of 5 wt% were prepared by dispersing CNC powder in DI water. The suspension was stirred for 5 h followed by sonication. The amount of ultrasonic energy applied to the suspension was 10,000 J/g CNC powder [11]. Afterwards, 40 g of the prepared 5 wt% CNC suspension was added to a 100 mL beaker while being stirred at 600 rpm. Consequently, varying amounts (ranging from 0.4 to 40 mL) of the prepared CTAB solution, depending on the desired weight fraction of CTAB/CNC, were added slowly to the beaker. The suspension was stirred for 2 h and centrifuged to obtain the modified CNC particles. To ascertain that no additional quaternary ammonium salts have remained on the surface of CNC particles, they were thoroughly washed with DI water and filtered up to 10 times, as needed, using grade 50 Whatman filter paper, each followed by centrifugation at 12,000 rpm for 15 min. The obtained precipitates were collected and freeze dried under vacuum for 48 h. The final product was ground using a mortar and pestle and sieved through a mesh (number 50, 297-micron) to yield a fine dry powder.

CNC modification was conducted using various amounts of CTAB to investigate the effect of surfactant on physical, chemical and dye adsorption characteristics of modified CNC. Eight different amounts of surfactant solution (5% CTAB solution) were added to the CNC suspension. These amounts are expressed as the weight ratio of CTAB to CNC, namely 0.01/1, 0.05/1, 0.1/1, 0.125/1, 0.25/1, 0.35/1, 0.65/1, and 1/1 w/w. These concentrations were chosen based on
preliminary trial experiments to form adsorbents that exhibit both positive and negative surface charges. Each sample is identified by MCNC followed by a number showing the weight fraction of CTAB/CNC used in its modification. For example, MCNC 0.25 is the modified sample in which the weight fraction of CTAB/CNC is 0.25 w/w.

4.3 Characterization methods

4.3.1 Rheological measurements

Rheological characterizations were carried out using an MCR 502 (Anton Paar) rotational rheometer with a cone-and-plate geometry (25 mm diameter, and 4° angle, gap size 0.047 mm). The independence of obtained results from the type of geometry (cone-and-plate or parallel plate) and gap size, used for rheological experiments, had been previously explored and reported in literature [4].

Steady shear was performed over the range 0.01 to 100 s\(^{-1}\) of shear rates (\(\dot{\gamma}\)) to obtain the viscosity behavior of pristine CNC suspensions. Amplitude sweep experiment was performed at a frequency of 1 HZ to determine the range of strains over which the samples show a linear viscoelastic behavior. Linear viscoelastic (LVE) amplitude sweep was performed over angular frequencies from 0.1 to 100 rad. s\(^{-1}\) in order to determine the viscoelastic properties of pristine and surfactant-added CNC suspensions. All rheological measurements were performed at 25 °C, and a thin film of silicon oil was applied to the edges of the geometry to prevent the evaporation of water. All reported figures are an average of 3 replicates. Error bars are not included in the plots to maintain clarity as they were smaller than the symbol sizes in all cases.
4.3.2 Zeta potential

Zeta potential measurements were conducted to investigate the effect of surfactants on the overall surface charge density of CNC particles within the suspensions, and the synthesized MCNC particles. As for the CNC suspensions, the zeta potential measurement was performed directly on the suspension of interest. As for MCNCs, 10 mg of the synthesized powder was dispersed in 50 ml DI water and stirred for 1 h to obtain 0.02 wt% suspension, similar to the dosage used for dye adsorption experiments. The zeta potential measurements were conducted using a Brookhaven NanoBrook Omni zeta potential analyzer on PALS mode. Each measurement was conducted 10 times over 50 cycles, and all the reported values are the average of 10 measurements. Since the error bars were smaller than the symbol sizes, they are not included in the graphs to maintain clarity.

4.3.3 Fourier transform infrared (FTIR) analysis

Fourier transform infrared (FTIR) analysis was performed to examine changes in the surface chemistry of CNC, and the interactions between the dye molecules and adsorbents. FTIR spectra for pristine CNC and treated CNC before and after adsorption were obtained using a PerkinElmer Frontier FT-IR in the wavenumber range of 650-4000 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\).

4.3.4 X-ray diffraction

Since the crystalline structure plays a prominent role in the reinforcing effects of CNC particles, X-ray diffraction was used to investigate the possible alterations in the crystalline structure of CNCs as a result of modification with CTAB. Furthermore, the XRD patterns would detect the existence of any remaining undesirable quaternary ammonium salts during the synthesis process.
X-ray diffraction was performed on unmodified CNCs and modified MCNCs with different weight fractions of CTAB using a Bruker D8 Advance diffractometer.

4.3.5 Scanning electron microscopy (SEM)

Scanning electron microscopy was conducted using a Hitachi S4700 field-emission SEM to investigate the effect of modification on the morphology of CNC particles, and the possible effect of morphology on the adsorption of Congo red.

4.3.6 Dye adsorption experiments

Adsorption experiments were conducted at room temperature by adding 10 mg of MCNCs adsorbent to 50 mL of a Congo red dye solution while being stirred at 600 rpm in a 100 mL beaker. The suspension was stirred for various amounts of time between 5 and 120 min. The suspension was then centrifuged at 8000 rpm for 15 min. After removing the adsorbent, the residual concentration of CR in the solution was determined by measuring the maximum absorption intensity, happening at 600nm for CR, using a Cary 100 UV-Vis spectrophotometer over the wavelength range of 200-1000 nm. The measured intensities were converted to concentration (mg L\(^{-1}\)) using the calibration curve of CR dye obtained through serial dilution of CR solutions over the range 1 to 400 mg L\(^{-1}\). The dye adsorption capacity of the adsorbents at contact time, \(t\) (min), was calculated using the following equation:

\[
q_t = \frac{(C_0 - C_t)V}{m} \tag{4.1}
\]

Where \(C_0\) (mg L\(^{-1}\)) is the initial dye concentration in the solution, \(C_t\) (mg L\(^{-1}\)) is the concentration of dye in the solution at time \(t\), \(V\) (L) is the volume of the dye solution, and \(m\) (g) is the mass of adsorbent added to the dye solution.
The percentage of removal was calculated by:

\[ \text{Removal} \% = \frac{(C_0 - C_t)}{C_0} \times 100 \]  

(4.2)

And the equilibrium adsorption capacity was calculated using:

\[ q_t = \frac{(C_0 - C_e)V}{m} \]  

(4.3)

Where \( C_e \) (mg L\(^{-1}\)) is the concentration of dye solution at equilibrium.

To study the kinetics of adsorption, a new dye solution was prepared for each contact time, and the concentration of CR was fixed to 100 mg L\(^{-1}\) in all experiments. Furthermore, the isotherm study was conducted over a dye concentration range of 50 to 400 mg L\(^{-1}\). All adsorption experiments were performed three times and the reported results are the average of three replicates.

### 4.3.7 Regeneration study of MCNC

The dye-loaded MCNCs were removed from the dye solution, after being agitated in 100 mg L\(^{-1}\) CR solution until the equilibrium was reached, by centrifugation. These dye-loaded MCNCs were then introduced into a beaker containing 200 mL of 100% Ethanol and stirred for 12 hours at 25°C with stirring speed of 100 rpm. After the desorption, MCNCs were washed and filtered following the same protocol as elaborated in the synthesis section and were used for the next cycles. A total number of 5 successive adsorption-desorption cycles were performed on the adsorbent.
Chapter 5: Rheology of CNC suspensions in the presence of surfactants

5.1 Shear rheology of pristine CNC suspensions

5.1.1 Steady-state shear viscosity profile

Figure 5.1 shows the steady-state shear viscosity of CNC suspensions as a function of shear rate at six concentrations, namely, 1, 2, 3, 4, 5 and 7 wt% at room temperature. Viscosity shows a significant dependence on the concentration as the viscosity at the lowest shear rate (0.1 s\(^{-1}\)) increases by 3 orders of magnitude when concentration changes from 1 to 7 wt%. At concentrations higher than 4 wt%, the samples exhibit a single shear thinning behavior over the whole range of considered shear rates, 0.01-100 s\(^{-1}\), and is well represented by a power law relationship, \( \eta = K \dot{\gamma}^{n-1} \) where \( n \) is the shear thinning exponent, and \( k \) is the consistency index, corresponding to the viscosity at \( \dot{\gamma} = 1 \text{ s}^{-1} \). The absolute value of \( n \) rises as the concentration increases implying the concentration dependence of the shear thinning exponent.

Steady-shear viscosity profiles are also used to explore the microstructure of CNC suspensions, at different concentrations, and the transitions from one microstructure to another with the change of concentration. Based on Figure 5.1, the viscosity profile of 1 wt% sample shows a Newtonian plateau at low shear rates followed by a shear thinning behavior at intermediate shear rates and a second plateau at high shear rates, typical of an isotropic sample. As for the samples of higher concentration, 2, 3 and 4 wt%, the steady shear exhibits a three-region behavior consisting of two shear thinning regions at high and low shear rates and one plateau in the intermediate shear rates. The distinction of these three regions becomes more tangible as the concentration decreases. This result implies the liquid crystalline behavior of CNC suspensions at these concentrations which stems from the formation of chiral nematic phases. At low shear
rates, the alignment of chiral nematic domains with shearing direction results in a shear thinning profile followed by a plateau at intermediate shear rates where all domains become oriented along the shearing direction. At high shear rates, the liquid crystal domains are destroyed by the applied stresses making it possible for every single nanorod to align with the shearing direction. As for the samples of higher concentration, 5 and 7 wt%, a single shear thinning behavior is observed over the whole range of shear rates attributed to the gelation of CNC suspensions at these concentrations, which prevents the development of chiral nematic phases.

![Steady-state viscosity (η), versus shear rate (γ) for CNC suspensions with concentration varying from 1 to 7 wt%](image)

**Figure 5.1:** Steady-state viscosity (η), versus shear rate (γ) for CNC suspensions with concentration varying from 1 to 7 wt%

### 5.1.2 Linear viscoelastic frequency sweep

Frequency sweep is performed to gain additional insight into the microstructure of the CNC suspensions at various concentrations, and the transitions between the microstructural states
(isotropic, chiral nematic, gel). Figure 5.2 shows the frequency sweep results at three different concentrations of CNC, 3, 4 and 5wt%.

![Figure 5.2](image)

**Figure 5.2**: Storage modulus ($G'$), and Loss modulus ($G''$) versus angular frequency ($\omega$) for 3 wt%, 4wt% and 5 wt% CNC suspensions

At 3wt %, the loss modulus ($G''$) of the CNC suspension is larger than the storage modulus ($G'$) at all examined angular frequencies ($\omega$) typical of a viscoelastic liquid. However, as the concentration of CNC increases to 4 wt%, the storage and loss moduli overlap over the whole range of angular frequencies indicating that transition from chiral nematic phase to gel starts to happen at this concentration. As for the higher concentrations, 5 wt%, the storage modulus ($G'$) exceeds the loss modulus ($G''$) at all frequencies, indicating behavior of a viscoelastic solid. This implies that CNC suspensions form a gel at concentrations higher than 4 wt%. Furthermore, as the concentration of CNC increases, the dependence of viscoelastic moduli on angular frequency
decreases which is inversely proportional to the stiffness of the gel formed. A similar rheological behavior was previously reported [51], [52].

The gelation of CNC suspension with increasing concentration is attributed to the decrease in electrostatic double layer distances between CNCs [11], [12]. Hence, the attraction forces between the hydroxyl groups (hydrogen bonds) of neighboring CNCs would form a network of crosslinks which encompasses the whole sample and ultimately forms the gel. The stiffness of the gel at higher concentrations of CNC is attributed to the stronger attractive forces between CNCs resulting from the increasing compactness of electrostatic double layers. In addition to hydrogen bonds, van der Waals forces could be another source of the attractive forces leading to gelation [53].

5.2 CNC suspensions with added surfactant

5.2.1 Effect of CTAB on rheology of CNC suspensions

Figure 5.3 shows the effect of CTAB on the storage modulus ($G'$) and loss modulus ($G''$) of 3 wt% CNC suspensions in the presence of various amounts of surfactant (0.2-6 mM). As previously discussed, pristine CNC suspension resembles a viscoelastic liquid at 3 wt% for which the value of storage modulus ($G'$) is less than the loss modulus ($G''$) over the whole range of angular frequency. Upon addition of CTAB, surfactant molecules are adsorbed to the surface of CNCs from their hydrophilic head, due to the electrostatic attractions between the positive head of CTAB and negative sites (sulfate ester groups) of CNCs, as shown in Figure 5.4. The adsorption of CTAB molecules on the surface of CNCs screens off the repulsion between these nanoparticles resulting in the compression of the double layer surrounding CNCs. In addition, the hydrophobic attraction between the tail sections of CTAB molecules contributes to the
attraction forces between two neighboring CNC particles. As a result, the CNC particles tend to aggregate due to the existence of this weak attraction force.

Figure 5.3: (a) Storage modulus ($G'$), and (b) loss modulus ($G''$) versus angular frequency ($\omega$) for 3 wt% CNC suspension in the presence of CTAB with concentrations 0.2 to 6 mM.

Figure 5.4: Schematic illustration of CNC/CTAB interaction.

Figure 5.5.a shows the frequency sweep results for the 3 wt% CNC suspensions with 0.2mM CTAB. At high angular frequencies, storage modulus, $G'$, is larger than loss modulus, $G''$, 
implying a viscoelastic solid behavior although at low angular frequencies, $G''$ is larger than $G'$. This result confirms a low level of entanglement within the CNCs, but there is no strong cross linking between them due to the weakness of the attractive forces.

Figure 5.5: Storage modulus ($G'$), and Loss modulus ($G''$) versus angular frequency ($\omega$) for 3 wt% CNC suspensions with (a) 0.2 mM, (b) 0.4 mM, (c) 0.8 mM, and (d) 2 mM CTAB

As the concentration of CTAB increases, more surfactant molecules are adsorbed to the surface of CNCs, which contribute to the attraction between adjacent particles. Therefore, stronger links
form in between CNCs resulting in the gelation of suspension. According to Figure 5.5.b and 5.5.c, at CTAB concentration of 0.4 mM and higher, CNC suspension exhibits a weak gel-like behavior where $G'$ is larger than $G''$ over the whole range of angular frequency although the viscoelastic moduli are strongly dependent on the angular frequency. Therefore, 0.4 mM is taken as the point where actual crosslinks form between CNCs. Based on Figure 5.5.d, with further increase in the concentration of CTAB, the CNC suspensions turn into a stronger gel with more powerful crosslinks, which result from the growing hydrophobic attractive forces between CNCs. As the concentration of surfactant increases above a critical concentration, CTAB micelles form on the surface of CNCs. These micelles that are bound electrostatically to the surface of CNCs are called admicelles (Figure 5.6).

Figure 5.6: Formation of CTAB admicelles on the surface of CNCs
As a result of admicelle formation on the surface of CNCs, the neighboring CNC particles are attracted to each other through electrostatic attraction between the positive heads of admicelles and negative parts of the adjacent CNC particle, (Figure 5.7). This attractive force is stronger than the weak hydrophobic attraction force, and it is happening at lower surfactant concentrations. Therefore, a quite strong network forms above this critical concentration and the difference between storage modulus ($G'$) and loss modulus ($G''$) becomes considerable (Figure 5.5.c). This critical concentration seems to happen between the CTAB concentrations of 0.6mM and 0.8mM, where the viscoelastic moduli are weakly dependent on the angular frequency.

Figure 5.7: Schematic of CNC aggregation due to the formation of admicelles

After a second critical surfactant concentration, the high level of entanglement among CNCs results in the formation of aggregates. According to Figures 5.3 and 5.5.d, above 2mM of surfactant concentration, the suspension shows a stiff gel-like behavior for which the viscoelastic
moduli are almost independent of angular frequency. At this stage, the CNC aggregates precipitate and are not stable. As a result, the gel formed becomes turbid.

As shown in Figure 5.3, further increase in the concentration of surfactant above 2mM does not significantly change the viscoelastic moduli of the formed gel. The reason could be attributed to the fact that above 2mM, the addition of surfactant will only lead to the formation of free micelles in the suspension (Figure 5.8), which do not have any considerable effect on the interactions between the CNC particles covered with surfactant. Accordingly, the second critical surfactant concentration lies between 1 mM and 2 mM. The formation of free micelles takes place at a concentration higher than the critical micelle concentration (CMC) of CTAB because the interactions between CNCs and CTAB molecules delays the formation of free micelles [50].

![Free micelle formation of CTAB](image)

**Figure 5.8: Free micelle formation of CTAB**

In order to gain a better understanding of the mechanism by which CTAB adjusts the rheological behavior of chiral nematic CNC suspensions, the effect of ionic strength was investigated on the
rheology and zeta potential of 3 wt% CNC suspensions and compared with the results obtained for CTAB. Figure 5.9 shows the effect of NaCl on the storage modulus ($G'$) and loss modulus ($G''$) of 3 wt% CNC suspensions at different salt concentrations (1-10 mM). Unlike CTAB, the storage modulus of CNC suspension drops considerably upon addition of NaCl. This decrease in the storage modulus is attributed to the electroviscous effects. In the rheological study of rigid Brownian particles, there exists three possible electroviscous effects contributing to the interactions between the particles and thus the viscosity [54]. These effects are: (1) the deformation of double layers around colloidal particles as a result of the applied shear, (2) overlapping of double layers under shearing, and (3) dimensional changes of the colloidal particles. In the case of CNCs, their highly crystalline structure makes dimensional changes impossible. However, previous studies have shown that increasing ionic strength by addition of NaCl results in the compression of the double layers surrounding CNCs. Therefore, the interactions (including both attractive and repelling forces) between CNCs with compressed double layers would become less [13]. Although the compression of repelling forces might decrease the hydrodynamic particle size, i.e. bringing the CNCs closer, it would not promote the development of a considerable attractive association between adjacent CNCs. Hence, the storage modulus decreases upon introducing NaCl to the CNC suspension.

Above 1mM, as the concentration of NaCl increases, the compression of double layers sets the stage for development of attractive forces between CNCs arising from the hydrogen bonds, between hydroxyl groups of CNCs, and van der Waals forces. These attractive forces are weaker at lower ionic strength and increase with the concentration of salt up to a point where the links between the CNCs form an interconnected network within the CNC suspensions, and it exhibits
a viscoelastic solid-like behavior at 6 mM NaCl. The transition from viscoelastic liquid to gel seems to be happening between salt concentrations of 4 mM and 6 mM. Further increasing the concentration of salt results in the continuous compression of double layer and contributes to the strength of strength and effectiveness of hydrogen bonds. Hence, the density of crosslinks rises to the point where the CNC suspension shows a stiff solid-like behavior at 8mM NaCl, and its storage modulus becomes almost independent of angular frequency. The storage modulus does not considerably increase from 8 to 10 mM salt concentration implying that the suspension reaches a relative equilibrium in terms of the effect of ionic strength on the viscoelastic moduli.

Figure 5.9: (a) Storage modulus ($G'$), and (b) loss modulus ($G''$) versus angular frequency ($\omega$) for 3 wt% CNC suspension in the presence of 1 to 10 mM NaCl

Zeta potential measurement was performed on CNC suspension in the presence of NaCl and CTAB to gain additional insight into the screening-off effect, surface charge alterations and prevailing rheology-modifying mechanisms caused by increasing the ionic strength and surfactant concentration. Based on Figure 5.10.a, the addition of NaCl decreases the negative
surface charge density of CNCs by screening-off the repulsive forces between sulfate-ester groups ($-O-SO_3^-$). Although the decrease in the negative charge density of CNCs takes place with a mild slope, an increase is observed in the values of measured storage modulus ($G'$) from 4 mM to 6 mM NaCl. This behavior could be attributed to the fact that the double layer surrounding CNCs is compressed with the addition of NaCl up to a point where the attractive forces overcome the repulsive barrier and become dominant throughout the suspension. Therefore, strong links (hydrogen bonds) form between CNCs resulting in gelation.

![Figure 5.10: Zeta potential versus the concentration of (a) NaCl, and (b) CTAB for 3 wt% CNC suspension](image)

In the case of CTAB, a similar trend is observed for the change in the values of zeta potential as the negative charge density decreases on the surface of CNCs (Figure 5.10.b). However, the concentration range of surfactant in this case is one-tenth of the NaCl concentration range despite both additives are monovalent cations. This observation implies that the formation of gel structure in the case of CTAB is not solely controlled by the screening-off effect. It further confirms the existence of attractive forces in addition to hydrogen bonding and van der Waals forces. Furthermore, the change in the storage modulus of CNC suspensions shows a stepwise
increase by CTAB addition implying the permanent existence of attractive forces which increase gradually with the concentration of surfactant. These results further prove the previous arguments regarding the existence of hydrophobic attractions, at lower surfactant concentrations, and strong electrostatic links between the surfactant-coated CNCs at higher surfactant concentration.

5.2.2 Effect of SDS on rheology of CNC suspensions

Previous studies on the interaction of SDS with negatively charged particles suggested that there are two possible attraction scenarios that could happen between surfactant molecules and CNCs. Hydrophobic attraction between the carbon tail of surfactant molecules and less charged areas on the surface of CNCs is one source of attractive forces. Secondly, it is possible that Na\(^+\) cations can serve as electrostatic bridges between the negative heads of surfactant molecules and surface of CNCs. In the first scenario, it is expected that extra repulsive forces would emerge which could result in larger negative surface charge density and, thus more repulsion between individual CNCs implying that the values of zeta potential will become more negative. As for the second scenario, it is believed that hydrophobic attraction between the carbon tails of CNC-bound surfactant molecules would establish attractive forces between CNCs which could act as crosslinks resulting in larger values of zeta potential and ultimately gelation of CNC suspension [55], [56]. To investigate the existence of these scenarios and their dominance, LVE frequency sweep was performed on CNC suspensions with various concentrations of SDS, between 0.2mM and 30mM. Due to the compactness of data points and for the sake of clarity, the values of complex modulus, G\(^*\), were calculated from the frequency sweep experiments and are plotted versus the concentration of SDS in Figure 5.11. G\(^*\) is used as a criterion to compare the strength
of attractive forces between CNCs. The frequency sweep results (viscoelastic moduli versus angular frequency) are only plotted for selected samples.

According to Figure 5.11, the change in the complex modulus of 3 wt% CNC suspension with the concentration of SDS shows a three-region behavior. First, the complex modulus, $G^*$, increases considerably and reaches an extremum at 0.25 mM SDS concentration. Then, it drops by almost an order of magnitude and reaches its minimum at 2mM. Afterwards, the complex modulus, $G^*$, shows a continuous upward trend with the concentration of SDS. This three-region behavior is attributed to the competition between the previously mentioned attractive forces, which set the stage for possible crosslinks between CNCs, and the innate repulsive forces between sulfate groups on the surface of CNCs. Upon addition of surfactant, SDS molecules could be adsorbed to the surface of CNCs from their hydrophobic tail. Concurrently, the second
possible scenario is the association of SDS molecules to the surface of CNCs from their negative head by bridging through Na⁺ cations. The former is expected to increase the repulsive forces between CNCs while the latter would screen them off.

In region I, the second scenario is believed to be dominant implying that surfactant molecules have screened-off the negative charges. Thus, CNC particles tended to aggregate, and the storage modulus, $G'$, and consequently, the complex modulus, $G^*$, have increased. The dominance of screening-off effect has also been confirmed by zeta potential measurement, plotted in Figure 5.12, which shows a decrease in the absolute value of zeta potential with increasing the concentration of SDS up to 0.25 mM.

![Zeta potential versus the concentration of SDS for 3 wt% CNC suspension](image)

Figure 5.12: Zeta potential versus the concentration of SDS for 3 wt% CNC suspension

Figure 5.13.a shows the viscoelastic moduli of 3 wt% CNC suspension versus angular frequency at 0.25 mM SDS. At high angular frequencies, $G' > G''$ while at lower frequencies, $G'' > G'$. This behavior is typical of uncrosslinked polymers and implies that the dominant attractive forces are not strong enough to result in the formation of crosslinks between CNCs. In region II,
the repulsive forces between the negative heads of tail-bound surfactant molecules overcomes the attractive forces between the hydrophobic tails of cation bridge-bound surfactant molecules. Therefore, the negative charge density has increased on the surface of CNCs leading to an increase in the absolute values of zeta potential, reaching a local extremum at 0.75 mM, and a decrease in complex viscosity, G*, where it shows a minimum at 2 mM SDS concentration.

Figure 5.13: Storage modulus (G'), and Loss modulus (G'') versus angular frequency (ω) for 3 wt% CNC suspensions with (a) 0.25 mM, (b) 3 mM, (c) 4 mM, and (d) 8 mM SDS
In region III, as the concentration of SDS increases over 2 mM, the complex modulus, $G^*$, rises by roughly two orders of magnitude and reaches a relative plateau. In this region, the attractive forces overcome the repulsive forces once more leading to the formation of stronger crosslinks between CNCs. Based on Figures 5.13.b and 5.13.c, gelation of 3 wt% CNC suspensions takes place somewhere between 3 mM and 4 mM SDS concentration. At 4 mM, the storage modulus, $G'$, is larger than the loss modulus, $G''$, over the whole range of examined angular frequencies, which implies the development of strong crosslinks between CNCs. The dominant attractive forces in this region could be hydrophobic attraction, cation bridging and hydrogen bonds. Above 4mM, further addition of SDS has resulted in the formation of a stronger network of crosslinks, and the viscoelastic moduli become less dependent on angular frequency. However, the zeta potential constantly increases after 0.75 mM SDS and reaches a plateau at 10 mM. This behavior could be attributed to the fact that as the concentration of surfactant increases, extra free SDS molecules and Na$^+$ are present in the suspension restricting the mobility of CNCs. Hence, the absolute values of zeta potential decreases.

To compare the degree and strength of crosslinking between CTAB-CNC and SDS-CNC complexes, values of storage modulus, $G'$, at the lowest examined frequency, 0.1 rad/s, was plotted versus the concentration of surfactant in Figure 5.14.

Based on Figure 5.14, it can be concluded that the degree of crosslinking is considerably higher in the case of CTAB as the values of storage modulus, $G'$, at $\omega=0.1$ rad/s, are larger comparing to the case of SDS by virtually one order of magnitude. This difference was already expected by considering the source of attractive forces in each case. As previously mentioned in addition to hydrophobic attraction and hydrogen bonds, electrostatic attraction is another factor responsible
for the formation of crosslinks between CNCs in the presence of CTAB, but no electrostatic attraction occurs between CNCs in the case of SDS. Furthermore, the screening-off effect of CTAB is greater, and therefore makes more contribution to the effectiveness and strength of hydrogen bonds (between hydroxyl groups of CNCs).

Figure 5.14: Storage modulus, $G'$, at $\omega=0.1$ rad/s versus (a) SDS and (b) CTAB concentration for 3 wt% CNC suspension
Chapter 6: Adsorptive removal of Congo red by surfactant modified cellulose nanocrystals

As previously discussed, the unique properties of CNCs have made them suitable for various applications among which dye adsorption had been particularly interesting in the recent years due to the abundance of different functional groups in the structure of CNCs providing active sites for the adsorption of industrial dyes. Although the high density of negative charges on CNCs prevents the adsorption of anionic dyes. In chapter 6 of this research work, a cationic surfactant, CetylTrimethylAmmonium Bromide (CTAB), was used to modify CNCs and synthesize a new adsorbent, following the procedure discussed in experimental section, that could improve the ability of CNCs to adsorb anionic dyes. Congo red is the model anionic dye used in this study.

6.1 Characterization of modified CNC (MCNC)

6.1.1 FTIR analysis

FTIR analysis was conducted to explore any alterations on the surface chemistry of CNCs. The FTIR spectra of MCNCs are depicted in Figure 6.1. After modification, new peaks appear at 2917-2919 cm\(^{-1}\) and 2850-2851 which are related to C-H stretching band. These bands are assigned to the –CH\(_3\) and –CH\(_2\) groups from the alkyl tale of CTAB molecule [18]. Furthermore, as the weight fraction of CTAB increases, these peaks intensify due to the presence of more surfactant molecules on the surface of CNCs. In addition, a weak intensity peak associated with –CH\(_2\) bending was observed at 1430-1463 cm\(^{-1}\) at higher concentrations of surfactant. Figure 6.2 shows the FTIR spectra of adsorbents after the adsorption process. Intense and apparent peaks were observed at 662 and 1610 cm\(^{-1}\) for all adsorbents associated with the \(\text{C} = \text{C}\) bending
vibrations and stretching, respectively, which corresponds to the phenyl groups in the structure of the CR dye [57]. These results confirm the successful adsorption of CR by the synthesized adsorbents.

![FTIR spectra of Pristine CNC, and MCNC 0.125, 0.25 and 0.65](image)

Figure 6.1: FTIR spectra of Pristine CNC, and MCNC 0.125, 0.25 and 0.65
6.1.2 XRD analysis

The peaks at 14°, 16°, 22.5° and 34.6° are present for all modified samples as seen in Figure 6.3. These peaks correspond to the planes 101, 10-1, 002 and 040, respectively, and correspond to the characteristic peaks of cellulose I in CNCs [58]. Based on the obtained results, this modification has not changed the crystalline structure of CNC particles and adjustments have only taken place on the surface of CNCs. Furthermore, it is concluded that all quaternary ammonium salts are successfully removed from the surface of CNC particles. This implies there are no excess CTAB that would be present upon addition of modified CNCs to the dye solution. The XRD patterns for the rest of the MCNC samples are included in the appendix Figure A.2.
6.2 Effect of modification on the surface charge of CNC particles

The surface charge of adsorbents play an important role in the adsorption of ionic dyes, such as Congo Red, since electrostatic attraction is one of the dominant adsorption mechanisms. Previous studies suggest that addition of surfactants to CNC suspensions would mainly result in alterations in the surface charge of CNC particles which could also affect the interactions between nanoparticles [16]. Therefore, modification with surfactants would probably affect the adsorption properties of CNCs to a great extent. The preliminary experiments indicated that pristine CNC does not adsorb CR due to the strong repelling forces attributed to the high negative charge density on the surface of CNC particles, thus leading to a zero adsorption capacity at all the examined agitation times and CR concentrations. Figure 6.4 shows the equilibrium adsorption capacities of CNCs modified with various amounts of CTAB. Addition of 0.01 w/w CTAB resulted in adsorption of CR with very low capacity, 12 mg of dye per g of
MCNC as the amount of surfactant has increased to 0.05 w/w, the adsorption capacity increased more than four times, 50 mg/g. Further addition of CTAB increased the adsorption capacity considerably to 172 mg/g at 0.1 w/w. The adsorption capacities exhibit a weak maximum at 0.25 w/w where the capacity is 237 mg/g. After this point, the adsorption capacities drop slightly to 216 mg/g and remain relatively constant even at higher CTAB concentrations. This behavior is attributed to the alterations taken place on the overall surface charge density of CNC particles.

![Graph showing the effect of CTAB weight fraction on the adsorption capacity of modified CNC](image)

**Figure 6.4:** Effect of CTAB weight fraction on the adsorption capacity of modified CNC - experimental conditions- dye concentration, 100 mg/L; dosage, 10mg/50cc; natural pH, 7.5; temperature, 25 °C; equilibrium time, 90 min.

To investigate the extent in the surface charge change of CNC particles, zeta potential measurements were performed since the zeta potential is proportional to the surface charge of the particles. Figure 6.5 depicts the zeta potential of CNC and MCNC samples.
Figure 6.5: Effect of CTAB weight fraction on Zeta potential of modified CNC

The pristine CNC suspension shows a zeta potential of -55 mV. Upon addition of CTAB to the CNC suspension, the cetyltrimethylammonium cations (CTA+) are adsorbed to the surface of the CNC particles with their cationic head facing towards the particles, Figure 6.6.a. This adsorption takes place due to the electrostatic attraction between the positively charged head of cetyltrimethylammonium cations and negatively charged sulphate ester groups on the surface of CNC particles [59]. As the concentration of CTAB increases, more surfactant molecules are adsorbed to the surface of CNC particles up to the point where the negative charges on the surface of CNCs are neutralized by the positive charges of the surfactant. At this point the zeta potential becomes zero. Further increase in the concentration of CTAB results in the formation of admicelles on the surface of CNC particles, as shown in Figure 6.6.b. This is attributed to the hydrophobic attraction between the hydrophobic tails of the bound and free surfactant molecules. Therefore, a surface charge reversal takes place, and the zeta potential becomes more positive as the surfactant concentration increases. Nevertheless, the surface of CNC particles saturates with
surfactant molecules at a critical concentration after which further addition of CTAB results in the formation of free micelles as depicted in Figure 6.6.c. This critical concentration is slightly larger than the critical micelle concentration (CMC) of CTAB, namely 1mM. In addition, this slight difference is attributed to the presence of CNCs in the medium postponing the formation of free micelles due to the adsorption of surfactant molecules [47], [60]. Hence, surfactant addition would not change the net surface charge of CNC particles after the critical concentration. In previous studies, a similar trend was observed for the change in the zeta potential of cellulosic surfaces, including films [47], fibers [48] and nanocrystals [49], as a result of their interaction with quaternary ammonium surfactants.

The equilibrium adsorption capacity exhibits a maximum at the optimum surfactant weight fraction of 0.25 w/w, at which the zeta potential value attains its highest value. After this point, both the zeta potential and equilibrium adsorption capacity drop slightly and remain roughly constant at higher surfactant weight fractions. This observation could be attributed to the fact that further addition of surfactant above 0.25 w/w would result in an increase of the overall ionic strength as well as into a rearrangement of the CNC bound surfactant molecules, admicelles, and free micelles [59]. As previously discussed, the synthesized adsorbent is thoroughly washed and dialyzed to remove all unbound surfactant molecules and thus none of these enter the dye solution. Depending on the extent of the modification, the dominant adsorption mechanism might be different for different modified samples. The adsorption mechanisms are discussed in detail below.
Figure 6.6: Schematic illustration of CTAB/CNC interactions
6.3 Adsorption kinetics

The adsorption kinetics of modified CNCs were investigated to explore the adsorption rate and rate-controlling factors in order to gain a better understanding of the mechanism of adsorption. The effect of time on the adsorption of Congo red is shown in Figure 6.7. Adsorption capacity has risen above 100 $mg \ g^{-1}$ in only 5 min. This severely rapid increase in the adsorption of CR is attributed to the abundance of active adsorption sites in the beginning, and the significant adsorption driving force resulting from the large difference between the concentration of dye molecules in the solution and the surface of the MCNC particles. The increase of the adsorption capacity continues with a modest slope for roughly 80 min and reaches a plateau which lasts up to about 90 min. This implies that over a short period after the beginning of the adsorption process, the remaining vacant sites become sterically hindered by the already bound dye molecules [61]. Therefore, the adsorption proceeds with a lower rate until it reaches equilibrium. It was observed that the adsorption capacity reaches its maximum, namely $q_e$, after 90 min, about the same for all samples. Although the adsorption of CR onto MCNC was monitored up to 200 min, the adsorbent starts desorbing the dye molecules after about 90 min and remains constant afterwards. Hence, was concluded that the adsorption equilibrium time for MCNC is about 90 min.
The adsorption kinetics was further analyzed by examining three kinetic models including, a pseudo-first order, a pseudo-second order, and intraparticle diffusion model. The pseudo-first order and pseudo-second order are two of the most commonly used models for investigating the mechanism of adsorption and determining the adsorption rate constants. The linear forms of these equations are expressed as:

\[
\ln(q_e - q_t) = \ln(q_e) - K_1 t \tag{6.1}
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6.2}
\]

Where \( q_e (mg \ g^{-1}) \) is the equilibrium adsorption capacity of modified CNCs, and \( K_1 (\text{min}^{-1}) \) and \( K_2 (g \ mg^{-1} \ \text{min}^{-1}) \) are the rate constants of pseudo-first order and pseudo-second order models, respectively. The obtained experimental data are fitted using Equations 6.1 and 6.2. The results are shown in Figure 6.8, and the equilibrium parameters and correlation coefficients \( (R^2) \) are summarized in Table 6.1.
Figure 6.8: Linear regression of adsorption kinetic models for MCNC 0.25, and 0.65. (a) pseudo-first order, (b) pseudo-second order. Experimental conditions- dye concentration, 100 mg/L; dosage, 10mg/50cc; natural pH, 7.5; temperature, 25°C.

For all modified CNC samples, the value of $R^2$ is almost equal to unity for the pseudo-second order model. Furthermore, the theoretical $q_e$ calculated using the pseudo-second order model
complies with the equilibrium capacities obtained from the experimental results listed in Table 6.1. Comparing these parameters with the ones obtained from the pseudo-first order model implies that the adsorption of Congo red dye by the modified CNCs can be well described by the pseudo-second order model.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experiment</th>
<th>Pseudo-first order kinetic model</th>
<th>Pseudo-second order kinetic model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$q_{e,exp}$ (mg g$^{-1}$)</td>
<td>$q_{e,cal}$ (mg g$^{-1}$)</td>
</tr>
<tr>
<td>MCNC 0.25</td>
<td>244</td>
<td>179</td>
<td>0.119</td>
</tr>
<tr>
<td>MCNC 0.65</td>
<td>219</td>
<td>120</td>
<td>0.115</td>
</tr>
</tbody>
</table>

Table 6.1: Adsorption kinetic parameters of CR onto MCNC 0.25, and MCNC 0.65

The intra-particle diffusion model was used to further investigate the adsorption mechanism of Congo red by modified CNC and examine any possible rate-controlling steps. The intra-particle diffusion model is expressed as:

$$q_t = K_i t^{\frac{1}{2}} + C$$  \hspace{1cm} (6.3)

where $K_i$ (mg g$^{-1}$ min$^{-0.5}$) is the rate constant of intra-particle diffusion model, and $C$ is a constant representing the extent of the boundary layer effect. As shown in Figure 6.9, the $q_t$ vs. $t^{\frac{1}{2}}$ exhibits a change in slope implying that surface adsorption is not the only mechanism controlling the adsorption process. In fact, the adsorption process consists of two steps. First, the dye molecules are transported from the bulk solution to the external surface of the adsorbent by boundary layer diffusion. At the second stage, the dye molecules diffuse from the external surface into the porous structure of the adsorbent giving rise to this two-stage adsorption process.
Figure 6.9. Intra-particle diffusion model of CR adsorption onto MCNC 0.25, and 0.65, experimental conditions- dye concentration, 100 mg/L; dosage, 10mg/50cc; natural pH, 7.5; temperature, 25°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>First stage</th>
<th>Second stage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_1$(mg g$^{-1}$)</td>
<td>$K_1$(mg g$^{-1}$ min$^{-0.5}$)</td>
</tr>
<tr>
<td>MCNC 0.25</td>
<td>93.33</td>
<td>21.28</td>
</tr>
<tr>
<td>MCNC 0.65</td>
<td>139.48</td>
<td>10.78</td>
</tr>
</tbody>
</table>

Table 6.2: Intra-particle diffusion parameters for adsorption of CR onto MCNC 0.25, and MCNC 0.65

The equilibrium parameters for the intra-particle diffusion model are listed in Table 6.2. The results indicate that none of the C values are zero at either stage indicating that intra-particle diffusion is not the sole dominant adsorption mechanism. Intra-particle diffusion plays an important role in the adsorption process. At the first stage, the value of the intra-particle
diffusion rate constant, $K_i$, is the highest for MCNC 0.25, which is most likely attributed to its larger surface charge density and more active adsorption sites compared to the other samples.

### 6.4 Adsorption isotherms

Adsorption isotherms were examined over the CR concentration range of $50-400 \text{ mg L}^{-1}$ to further investigate the mechanism of adsorption and evaluate the adsorption properties of modified CNCs. In this study, two classic isotherm models, Langmuir and Freundlich, were used to determine the equilibrium isotherm parameters of the adsorbent.

The Langmuir isotherm describes a monolayer adsorption process with homogenous distribution of the adsorption sites on the surface of the adsorbent. The linear form of the Langmuir model is expressed as:

$$
\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L}
$$

(6.4)

Where $C_e (\text{mg L}^{-1})$, is the equilibrium concentration of the dye solution, $q_e (\text{mg g}^{-1})$ is the adsorption capacity at equilibrium, and $q_m (\text{mg g}^{-1})$ is the maximum amount of CR adsorbed per unit mass of adsorbent.

The Freundlich isotherm is an empirical model assuming that the adsorption process is a multilayer process and takes place on heterogenous surfaces [62]. The linear form of this model is:

$$
\ln(q_e) = \ln K_F + \frac{1}{n} \ln C_e
$$

(6.5)

Where $K_F (\text{L mg}^{-1})$ is a Freundlich constant related to the adsorption capacity, and $1/n$ corresponds to the heterogeneity of the adsorption surface, indicating the favorability of the adsorption process.
Figure 6.10. Linear regression of isotherm models for adsorption of CR onto MCNC 0.25 at 298, 308, and 318 K. (a) Langmuir, (b) Freundlich. Experimental conditions—dosage, 10mg/50cc; natural pH, 7.5.
The isotherm study was conducted on the optimum sample, MCNC 0.25, at three temperatures to investigate the temperature effect on the maximum adsorption capacity, simultaneously. The experimental data were fitted to both isotherm models, and the results are presented in Figure 6.10. The isotherm parameters and correlation coefficients ($R^2$) are summarized in Table 6.3. Based on the obtained results, the values of $R^2$ are larger than 0.994 at all temperatures indicating that the Langmuir model provides a better description of the adsorption isotherm. Furthermore, the theoretical $q_m$ values calculated from Langmuir model are in good compliance with the experimentally obtained $q_m$ values. This implies that the adsorption of CR onto MCNC is mostly monolayer, and the adsorption sites on the surface of the adsorbent are identical. In addition, the $q_m$ and $K_L$ values decrease with temperature indicating the exothermic nature of the adsorption process.

According to Freundlich model, the value of heterogeneity constant ($1/n$) was calculated to examine the favorability of the interaction between dye molecules and adsorbent. Based on the

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Langmuir model</th>
<th>Freundlich model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_m$ (mg g$^{-1}$)</td>
<td>$K_L$ (L mg$^{-1}$)</td>
</tr>
<tr>
<td>298</td>
<td>448.43</td>
<td>13.89</td>
</tr>
<tr>
<td>308</td>
<td>436.68</td>
<td>8.80</td>
</tr>
<tr>
<td>318</td>
<td>432.90</td>
<td>5.65</td>
</tr>
</tbody>
</table>

Table 6.3: Isotherm parameters of Langmuir and Freundlich model for the adsorption of CR onto MCNC 0.25
results listed in Table 6.3, the values of \(\frac{1}{n}\) are in the range of 0-1 and increase with temperature implying that the adsorption process is favorable at all temperatures, and the increase of temperature is not in favor of the adsorption process. In addition, the values of the Freundlich constant, \(K_F\), decrease with temperature, which further supports the exothermic nature of the adsorption process.

Table 6.4 shows the value of maximum experimental adsorption capacity \(q_{m,exp}\) of Congo red on several cellulose based adsorbents synthesized in the recent years. Based on Table 6.4, the maximum adsorption capacities are in the range of 40-600 mg/g which implies that MCNC is a suitable and comparable adsorbent for the adsorption of CR in aqueous medium.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>(q_m) (mg g(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTAB modified CNC</td>
<td>448</td>
<td>Present work</td>
</tr>
<tr>
<td>Imidazolium ionic liquid modified cellulose</td>
<td>563</td>
<td>[2]</td>
</tr>
<tr>
<td>Magnetic nanocellulose based ionic liquid</td>
<td>131</td>
<td>[33]</td>
</tr>
<tr>
<td>Crosslinked cellulose dialdehyde</td>
<td>42.03</td>
<td>[63]</td>
</tr>
<tr>
<td>Cellulose/Chitosan composite</td>
<td>381.7</td>
<td>[64]</td>
</tr>
<tr>
<td>CTAB impregnated chitosan hydrogel</td>
<td>271.74</td>
<td>[65]</td>
</tr>
<tr>
<td>Poly((N,N)-dimethylacrylamide-(co)-acrylamide) grafted hydroxyethyl cellulose hydrogel</td>
<td>102.4</td>
<td>[66]</td>
</tr>
</tbody>
</table>

Table 6.4: Maximum adsorption capacity for CR on various cellulose based adsorbents
To study the effect of temperature on the adsorption of CR by modified CNC, the thermodynamics of the system was analyzed at three temperatures, 25, 35 and 45°C over the concentrations 100-400 mg L⁻¹. The thermodynamic parameters calculated, included are the enthalpy ($\Delta H^0$), the entropy ($\Delta S^0$) and the Gibbs free energy ($\Delta G^0$). These were determined by using the following equations:

$$\Delta G^0 = -RT \ln K_C$$  \hspace{1cm} (6.6)

$$\ln K_C = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$$  \hspace{1cm} (6.7)

Where $R$ (8.314 J mol⁻¹ K⁻¹) is the ideal gas constant, $T$ (K) is the absolute temperature and $K_C$ is the Langmuir constant. Based on equation 6.7, $\Delta H^0$ and $\Delta S^0$ are calculated using the slope and intercept of the linear plot $\ln K_C$ vs. $1/T$.

The values of the thermodynamic parameters and Langmuir constant at each temperature are summarized in Table 6.4. Based on the results in Table 6.4, the negative values of Gibbs free energy at three experimental temperatures imply that the adsorption of Congo red onto modified CNC is spontaneous. Furthermore, as the temperature increased from 298 to 318 K, the absolute values of Gibbs free energy decreased meaning that adsorption process is more favorable at lower temperatures. Generally, the value of Gibbs free energy between 0 and -20 kJ/mol indicates that the adsorption mechanism is physisorption, while the value in between -80 and -400 kJ/mol indicates a chemisorption process. Based on the values of $\Delta G^0$ in Table 6.5, the adsorption of CR by modified CNC involves both chemisorption and physisorption. The values of $\Delta H^0$ and $\Delta S^0$ are found from the plot of $\ln K_C$ vs. $1/T$ to be equal to -35.45 kJ/mol and 0.018 J
K⁻¹ mol⁻¹, respectively. The negative value of $\Delta H^0$ reveals the exothermic nature of the adsorption process.

<table>
<thead>
<tr>
<th>$T(k)$</th>
<th>$Q_m$ (mg g⁻¹)</th>
<th>$K_L$ (L mg⁻¹)</th>
<th>$\Delta G^0$</th>
<th>$\Delta H^0$</th>
<th>$\Delta S^0$</th>
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</thead>
<tbody>
<tr>
<td>298</td>
<td>448.43</td>
<td>13.89</td>
<td>-23.66</td>
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<td>318</td>
<td>432.90</td>
<td>5.65</td>
<td>-22.85</td>
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<td></td>
</tr>
</tbody>
</table>

Table 6.5: Thermodynamic parameters of CR adsorption onto MCNC 0.25

6.6 Adsorption mechanism

Electrostatic attraction is one of the most effective factors in the adsorption mechanism. Based on the values of zeta potential for modified CNC samples plotted in Figure 6.5, the overall charge on the surface of modified CNCs are positive at CTAB weight fractions larger than 0.25 w/w, indicating that electrostatic attraction between the negative heads of CR and positive sites of MCNC is responsible for the adsorption of CR. However, at weight fractions lower than 0.125 w/w, the overall charge density on the surface of MCNC is negative indicating that CR molecules should be repelled, and adsorption of CR should not have happened. Nevertheless, the adsorption capacity of MCNC is not zero even at 0.01 w/w of CTAB implying that adsorption is practically happening despite the negative charge density on the surface of MCNC. This suggests that electrostatic attraction is not the sole mechanism of adsorption, and other mechanisms are also involved in the adsorption process. Furthermore, the amount of CTAB used in the modification step might affect the existence or dominance of each mechanism.
To explore the existence of various adsorption mechanisms, FTIR spectra of CR and the optimum sample, MCNC 0.25, are investigated before and after adsorption (Figure 6.11). Based on Figure 6.11, the extensive absorption peak at 3340 $cm^{-1}$, corresponding to the $-\text{OH}$ stretching vibration of MCNC slightly shifted, intensified and expanded after adsorption. The absorption peak at 3468, corresponding to the $-\text{NH}_2$ groups of CR, diminishes after adsorption. This verifies that hydrogen bonding is one of the major mechanisms involved in the adsorption of CR onto MCNC. In addition, two adsorption peaks at 1179 and 1222, corresponding to the sulfonate groups ($\text{SO}_3^-$) of CR, slightly shift and diminish considerably after adsorption. This implies that sulfonate groups of CR are involved in the adsorption process through electrostatic attraction with the positive heads of the bound micelles, namely $\text{N}^+$. Hydrophobic attraction between CR and the alkyl tale of single CTA+ molecules, bound to the surface of CNCs, is believed to be another mechanism engaged in the adsorption of CR onto MCNC. This would be the case especially at low weight fractions of CTAB where the zeta potential (Figure 6.5), suggests that the abundance of single CTA+ molecules bound to the surface of CNC is more than the bound micelles. Hence, compared to electrostatic interactions, hydrophobic attraction plays a more important role in the adsorption process for samples with negative zeta potential. Similar to the samples with positive zeta potential, hydrogen bonding is another mechanism responsible for the adsorption of CR onto MCNC when the overall charge density on the surface of adsorbent particles is negative.
The morphology of the adsorbent is another factor that influences the adsorption process. The intraparticle diffusion kinetic model suggested that the morphology of MCNC might play an important role in the adsorption process. To examine the morphology of MCNC and its potential effect on the adsorption of CR, SEM images of MCNCs were taken at different weight fractions of CTAB, Figure 6.12.
The SEM graphs reveal that addition of CTAB have resulted in the aggregation of CNCs in the form of fluffy bundles even at the lowest weight fraction of CTAB (MCNC 0.01), Figure 6.12.a. As the concentration of CTAB increases, the CNC aggregates form a layered structure with bigger particles, as depicted in Figure 6.12.b. Finally, at the optimum weight fraction of CTAB (MCNC 0.25), the CNC aggregates have formed a porous structure, Figure 6.12.d, which could be responsible for the intra-particle diffusion of dye molecules into the adsorbent particles.

Figure 6.12. SEM micrographs of MCNC (a) 0.01, (b) 0.05, (c) 0.125, (d) 0.25
Furthermore, based on the scales shown on the SEM micrographs, the increase in the size of the MCNC particles with addition of surfactant could be inferred.

![Diagram](image)

**Figure 6.13. Polymer induced micellization of CNC rods**

As previously discussed, the addition of CTAB to CNC suspensions results in the formation of admicelles on the surface of the particles above a critical concentration. The electrostatic attraction between the positive heads of the admicelles on one CNC particle with the negative parts of its neighboring particles would result in the formation of CNC bundles as depicted in Figure 6.13. The aggregation of CNCs, referred to as polymer induced micellization, generates pore areas between the particles which set the stage for the intra-particle diffusion of dye molecules into the adsorbent. Figure 6.14 shows the schematic of the existing mechanisms during the adsorption of CR onto MCNC.
Figure 6.14. Schematic of various active adsorption mechanism during the adsorption of CR onto MCNC

6.7 Adsorbent stability in aqueous environment

MCNCs were washed several times to remove unbound surfactant molecules on the surface of the CNC particles, and thus the adsorbent does not introduce any surfactant molecules into the solution. The number of cycles required to wash all the unbound surfactant molecules from the surface of MCNC depends on the amount of surfactant used for the modification. The existence of unbound surfactant molecules was examined by comparing the XRD patterns of MCNC with
pure CTAB. The XRD patterns that did not exhibit any intensity peaks, corresponding to the crystals of CTAB, were concluded to be free of unbound surfactant molecules. Table 6.6 shows the number of washing cycles required for different MCNC samples.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>MCNC 0.01</th>
<th>MCNC 0.05</th>
<th>MCNC 0.1</th>
<th>MCNC 0.125</th>
<th>MCNC 0.25</th>
<th>MCNC 0.35</th>
<th>MCNC 0.65</th>
<th>MCNC 1</th>
</tr>
</thead>
<tbody>
<tr>
<td># Required washing cycles</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>4</td>
<td>4</td>
<td>6</td>
<td>7</td>
</tr>
</tbody>
</table>

**Table 6.6: Number of required washing cycles during synthesis process**

MCNC 0.35 and MCNC 0.65 were chosen for further investigation on the effect of successive cycles of washing on the adsorption capacity of adsorbent. Figure 6.15 shows the change in the equilibrium adsorption capacity of MCNC 0.35 and MCNC 0.65 with the number of washing cycles. The samples contain a large amount of CTAB crystals right after the synthesis as the XRD patterns exhibit strong peaks corresponding to the characteristic peaks of CTAB, Figures A.3.b and A.3.c, implying the presence of free surfactant molecules in the samples. Therefore, other than the adsorption of CR by modified CNC particles, the surfactant and CR molecules are attracted to each other by electrostatic forces resulting in the precipitation of CR-CTAB complex. Before starting the washing cycles, MCNC 0.35 and 0.65 exhibit an equilibrium capacity of 288.44 and 312.36 mg/g, respectively. While washing cycles proceed, free surfactant molecules are removed gradually from the synthesized MCNC indicating that the apparent adsorption capacity would reduce. This downward trend in the adsorption capacities continue until the sample reaches the maximum number of required washing cycles. After this point, the adsorbent does not show any considerable changes in the adsorption capacity, and $q_e$ remains
roughly constant despite extra successive washing cycles. These results confirm the stability of MCNC in aqueous environment and against successive dialysis cycles.

![Graph](image)

Figure 6.15. Effect of successive washing cycles on the equilibrium adsorption capacity of (a) MCNC 0.35 and (b) MCNC 0.65- experimental conditions- dye concentration, 100 mg/L; dosage, 10mg/50cc; natural pH, 7.5; temperature, 25 °C; equilibrium time, 90 min.
Regeneration and reusability of a dye adsorbent is an important factor in evaluating its commercial applicability. To study the recyclability of MCNC, 5 cycles of adsorption/desorption were carried out on the optimum sample, MCNC 0.25, using ethanol, and the adsorption capacity was measured at the end of each cycle. Based on the results shown in Figure 6.16, it can be seen that MCNC has managed to recover over 85% of its original capacity after 5 cycles implying its good desorption ability. Hence, the regeneration study indicated that MCNC could be considered as an efficient adsorbent for the removal of dyes.

![Figure 6.16. Reusability of MCNC for CR adsorption](image)

Figure 6.16. Reusability of MCNC for CR adsorption
Chapter 7: Conclusions and Recommendation for future work

7.1 Conclusions

The rheology of chiral nematic CNC suspensions was studied in the presence of a cationic surfactant, CTAB, and an anionic surfactant, SDS. CTAB results in gradual gelation of CNC suspensions as it promotes attractive forces between CNCs. The nature of these attractive forces is hydrophobic, at low surfactant concentrations, and electrostatic, at high concentration. However, the complex modulus has shown a three-region behavior in the case of SDS indicating the existence of both attractive and repulsive forces at different concentration of surfactant whose dominance controlled the viscoelastic properties of CNC suspensions.

Surfactant modified CNC-based adsorbent was synthesized and used to examine its effectiveness for the adsorption of anionic dye, Congo red. The characterization of synthesized adsorbent implied that alterations have only taken place on the surface of CNCs where the surfactant molecules had been adsorbed through electrostatic attraction between the positive heads of CTAB and negative sites of CNCs. As the weight fraction of surfactant increased, the number of micelles and single CTA+ molecules, bound to the surface of CNCs, increased. This resulted in a reduction in the negative charge density of CNC particles up to a point where the charge density became positive. The samples exhibited an optimum at which the zeta potential and equilibrium adsorption capacity exhibited their maximum values. The experimental data were described well with both a pseudo-second order and intra-particle diffusion model indicating the existence of film-diffusion and intra-particle diffusion. This hypothesis was further supported by investigating the microstructure of MCNC showing its porous morphology. Isothermal studies at 298, 308, and 318 K on the optimum adsorbent concentration showed that the adsorption of CR
onto MCNC is exothermic and spontaneous and is well described by the Langmuir model. The adsorption process was concluded to involve both chemisorption and physisorption through several mechanisms including electrostatic attraction, hydrogen bonding, and hydrophobic attraction. Furthermore, it was discussed that the dominance of each mechanism depends on the amount of surfactant used for CNC modification. The adsorbent has shown great stability in aqueous environment under successive dialysis cycles. In addition, the regeneration study promoted MCNC as a promising reusable adsorbent as it recovered over 85 percent of its original adsorption capacity after 5 cycles of sorption and desorption.

7.2 **Recommendations for future work**

- This study focused on the gelation of chiral nematic CNC suspensions in the presence of one anionic and one cationic surfactant. Investigating the effect of surfactants on the rheology and physiochemical properties of isotropic CNC suspensions would also be of interest. Furthermore, other surfactants including neutral ones can be used to explore their influence on the rheology of CNC suspensions.

- As for the adsorption properties of CTAB-modified CNC, the main objective was to investigate the mechanism of adsorption and the procedure by which CTAB contributes to the anionic dye adsorption of CNCs. In future works, investigating the effect of environmental variables, such as pH of dye solution, on the adsorption properties of MCNC and their potential in the adsorption of other anionic dyes would be of interest. Furthermore, other anionic and cationic surfactants, such as SDS, can be used to modify CNCs and improve their adsorption properties.
References


[38] L. Wang and A. Wang, “Adsorption properties of Congo Red from aqueous solution onto


[53] M. El Achaby Nassima El Miri Hassan Hannache Said Gmouh Vera Trabadelo Adil


Appendices

Appendix A

Figure A.1: FTIR spectra of Pristine CNC, and MCNC 0.01, 0.05 and 0.1
Figure A.2: XRD pattern of Pristine CNC, MCNC 0.01, 0.05, and 0.1
Figure A.3: XRD Pattern of (a) CTAB, (b) MCNC 0.35 (unwashed), and (c) MCNC 0.65 (unwashed)