ABSTRACT

Thesis Title: Production of nanofibrillated cellulose from agrowaste residues and its application in phosphate removal from wastewater

Phosphorus is essential for many biological processes and agricultural productivity, playing a key role in energy transfer, nucleic acid synthesis, and plant growth. However, it's primary source i.e., phosphate rocks is a finite and non-renewable resource. Current estimates suggest that global reserves may be depleted within the next 150 years due to overexploitation and inefficient utilization. Concurrently, rapid urbanization and burgeoning industrial and agricultural activities have significantly increased phosphorus discharge into aquatic environments, leading to eutrophication, harmful algal blooms (e.g., red tides), and widespread ecological degradation. Given these challenges, the development of effective strategies for phosphorus removal and recovery from wastewater is crucial to ensure long-term environmental sustainability and the conservation of vital resources. This thesis focuses on exploring sustainable phosphate removal approaches using environmentally friendly, economically viable adsorbents that can easily be produced and tailored to enhance their selectivity toward phosphate anions. Nanofibrillated cellulose (NFC), derived from lignocellulosic biomass, presents a promising solution due to its renewable nature, biodegradability, high specific surface area, abundance of modifiable hydroxyl groups, and economic feasibility. However, traditional NFC production methods often involve high energy consumption, intensive use of strong acid/alkali pretreatment steps and generation of corrosive byproducts, thus limiting their environmental viability. To address these challenges, this work employs acidic natural deep eutectic solvents (NADES) combined with acetosolv as greener alternatives for the efficient fractionation of biomass into its constituent components; cellulose, hemicellulose, and lignin. The isolated cellulose is subsequently subjected to high intensity

ultrasonication for depolymerization into NFC. Thereafter, the resulting NFC is strategically modified through various approaches to optimize its phosphate adsorption capacity. This study offers a novel integrated approach to sustainable waste management and phosphate recovery from wastewater, contributing to the broader goals of environmental protection, circular economy, and resource resilience.

Chapter 1 underscores the vital importance of phosphate as an essential nutrient for all living organisms and its widespread applications in agriculture, industry, and domestic sectors. It outlines the primary natural sources of phosphate, mainly apatite minerals, predominantly found in countries such as Morocco, China, and the United States. The chapter also reviews global phosphate consumption trends based on data from international agencies. Furthermore, it provides an overview of phosphate reserves in various Indian states, including estimates of their quantities. To aid comprehensive understanding, the physicochemical properties of phosphorus and its biogeochemical cycle are discussed in detail. The chapter highlights growing concerns over the depletion of phosphate reserves due to overexploitation and inefficient use, which may contribute to environmental challenges such as reduced water quality and ecological imbalance. It examines key sources of phosphate pollution, wastewater discharge and compares different phosphate removal methods, emphasizing adsorption as a simple, cost-effective, and efficient approach. The chapter further explores the potential of sustainable adsorbents, particularly NFC produced from agro-waste residues such as sugarcane bagasse. It provides an overview of existing literature on NFC, detailing its production methods with an emphasis on green and environmentally friendly techniques. This chapter also presents the rationale for using NFC as an adsorbent, owing to its outstanding properties and promising application in wastewater treatment. Additionally, the chapter highlights the motivation behind the study and clearly states the objectives of the thesis, providing a foundation for understanding the overall structure and direction of the research.

In **Chapter 2**, This chapter summarizes the materials and experimental methods used to produce, modify, and evaluate the biomaterial, including procedures for phosphate adsorption studies. The specifications and purity of the chemicals utilized in the production and modification routes are provided. Several characterization methods, including TGA-DTG, XRD, FT-IR, HR-SEM, EDS, TEM, XPS, BET-surface area, DLS, and pH_{PZC}, were used to investigate the physicochemical properties of pristine NFCs and its modified form. Additionally, expressions for isotherm and kinetic models, and thermodynamics have been detailed that help to elucidate the adsorbate-adsorbent interactions and underlying adsorption mechanisms.

Chapter 3 emphasizes sustainable production of NFC from lignocellulosic agricultural waste, specifically sugarcane bagasse (SCB). Four acidic NADES were synthesized and evaluated as pretreatment agents in combination with the acetosolv method to enhance cellulose recovery. The Gly-CA NADES with acetosolv yielded the highest cellulose recovery (84.4%), followed by Xyl-CA (82.2%), Gly-TA (75.6%), and Xyl-TA (68.9%). Subsequent implementation of high-intensity ultrasonication (HIU) process resulted in rapid nanofibrillation with minimal cellulose loss. Morphological analysis using HR-SEM demonstrated fibrillated structure and reduction in diameter after treatment and, TEM and DLS analysis revealed NFCs with diameters of 30 – 35 nm and length in micrometre range, indicating an overall effective fibre disintegration. Structural characterization through XRD, FT-IR, and TGA/DTG confirmed that the cellulose structure remained intact even after pretreatment.

In **Chapter 4**, cationic adsorbent was developed by modifying the agrowaste-derived NFC with cetyltrimethylammonium bromide (CTAB) using facile quaternization method. Characterization techniques including pH_{PZC}, zeta potential, XRD, FTIR, HR-SEM, SEM-EDX, BET, and XPS confirmed the successful modification of NFC through the introduction of quaternary ammonium groups, which significantly enhanced its surface charge and affinity for phosphate ions. The cationic NFC showed a nearly threefold improvement in phosphate removal efficiency (~ 85 %) due to increased surface area and active sites. The adsorption process followed pseudo-second-order kinetic and Sips isotherm model, with maximum adsorption capacity of 21.78 mg/g, reaching equilibrium within 120 minutes. Besides, the adsorbent displayed stable adsorption capacity at wide range of pH attributed to its increased surface charge and PZC value. Furthermore, it exhibited excellent stability with only 12.61 % desorption rates over three cycles. Both XPS and FTIR results revealed that electrostatic adsorption (based on Lewis acid-base principle) and hydrogen bonding were primary adsorption mechanism.

Chapter 5 explores the effectiveness of bio-based polymer and clay composite comprising NFC and bentonite (BN) clay, synthesized in different mass ratios, for phosphate removal. Preliminary evaluations identified the NFC_1/BN_1 composite outperformed both its individual components and other composite variants in phosphate adsorption efficiency. To enhance its adsorption performance, the optimized NFC/BN composite was doped with magnesium ions, known for their high affinity toward phosphate. The resulting Mg@NFC/BN composite was comprehensively characterized using analytical techniques such as XRD, FT-IR, FESEM, EDX, XPS, and pH_{PZC} analysis. The hybrid composite demonstrated a maximum phosphate adsorption capacity of 19.2 mg/g and removal efficiency of 88.6% at initial phosphate concentration of 20 mg/L and adsorbent dose of 1 g/L. Equilibrium was reached within 90 minutes at 298.5 K. The composite also maintained high adsorption performance across a broad pH range and exhibited strong selectivity for phosphate even in the presence of competing anions. Adsorption kinetics followed a pseudo-second-order model, while the Langmuir isotherm best described the adsorption behaviour. Thermodynamic analysis confirmed the process as spontaneous and exothermic. The improved phosphate removal efficiency is attributed to a synergistic mechanism involving protonation, electrostatic attraction, and ligand exchange, promoting inner-sphere complexation. Furthermore, the phosphate-laden composite exhibited excellent water retention properties, enhancing soil moisture content and reducing evaporation which can be beneficial particularly in arid and semi-arid regions.

Chapter 6 provides a comprehensive summary and outlines the future prospects of this research. Based on the outcomes, the thesis presents an integrated and sustainable approach that utilizes waste lignocellulosic biomass wastes to produce NFC through green methods and subsequently utilizing the produced NFC (through strategic modification) for the removal and recovery of phosphate from wastewaters. Here, a synergistic combination of citric acid-based natural deep eutectic solvents (NADES) and the acetosolv process enabled the recovery of over 80% cellulose with minimal degradation. Among the modified NFC materials, CTAB-functionalized NFC demonstrated superior adsorption performance, with maximum phosphate adsorption capacity of 21.78 mg/g and demonstrates effective performance across a wide pH range making it suitable for real-world wastewater treatment applications. CTAB@NFC adsorbent also showed excellent stability across three desorption cycles, maintaining phosphate retention. Due to the inherent antimicrobial properties of CTAB and high surface area of NFC, CTAB@NFC can also be explored for antimicrobial applications, where immobilized CTAB remains effective against microbial contaminants. Furthermore, Mg@NFC/BN composite also exhibited a notable phosphate adsorption capacity of 19.2 mg/g. Beyond adsorption, the phosphate-loaded composite holds potential for soil applications, serving as a slow-release fertilizer while also improving water retention, owing to the hydrophilic nature of cellulose and the high porosity of BN. Overall, this work effectively integrates waste valorisation with wastewater treatment, offering a sustainable and holistic solution that contributes to environmental sustainability and resource management. In addition, the future perspectives of thesis are also emphasized that focus on green modification agents, multifunctional composites, pilot-scale trials, and integration into circular bioeconomy frameworks.