The Thesis of the Doctoral (Ph. D.) Dissertation

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ASSESSMENT OF NOVEL ADSORBENTS FOR THE SEQUETRATION OF POLLUTANTS FROM AQUEOUS SOLUTIONS – A SUSTAINABLE APPROACH TOWARD ENVIRONMENTAL MANAGEMENT

By

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1. BACKGROUND OF THE WORK AND ITS AIMS

1.1. Introduction

The remediation of heavy metals and pharmaceutical compounds from industrial wastewater is a subject of considerable environmental significance, attributable to their persistence within aquatic systems and the resultant detrimental impacts they exert on the environment. The enduring presence of contaminants like heavy metals and pharmaceuticals, coupled with their adverse consequences, underscores the critical importance of their removal from wastewater streams (Li et al., 2023). Potential Toxic Elements (PTEs) such as zinc, lead, copper, and cadmium are known for their hazardous effects, characterized by bioaccumulation, high toxicity, and non-biodegradability. The uncontrolled release of these pollutants has contributed to a global crisis, with over 40% of the world's lakes and rivers estimated to be contaminated by PTEs (Zamora-Ledezma et al., 2021). Furthermore, a recent investigation by the World Health Organization (WHO) revealed that approximately 2.2 million individuals die each year from illnesses caused by ingesting contaminated drinking water (Rind et al., 2024).

To address this issue, numerous technologies have been applied, including chemical precipitation, membrane filtration, and ion exchange. However, researchers have acknowledged the potential disadvantages of these conventional methods, including their high cost, the generation of hazardous secondary sludge, and their potential inability to effectively remove PTEs at low concentrations (Mishra et al., 2024). In contrast to these limitations, adsorption has been identified as a highly effective and easily implementable approach for the bioremediation of polluted water (Batool et al., 2018). Consequently, the global research trend is now focused on developing and applying inexpensive, ecofriendly, widely available, and efficient adsorbents.

This thesis investigates two novel adsorbents: Norway Spruce Wood Residue (NSWR) for the removal of four key heavy metals (Pb, Zn, Cu, Cd), and sub-bituminous coal chemically modified with sulfuric and nitric acids for the removal of the pharmaceutical Ciprofloxacin (CFX). These materials were selected for their low cost, widespread availability, and distinctive properties that make them promising candidates for sustainable environmental management.

The research also addresses the treatment of laundry water, a pertinent example of complex wastewater challenges. Laundry wastewater, originating from industrial and commercial establishments, is characterized by significant levels of turbidity, COD, BOD, and high pH, making it unsuitable for direct discharge or reuse without treatment. Its complex composition contributes to potential aesthetic losses and ecosystem toxicity, highlighting the critical need for effective and sustainable treatment technologies.

1.2. Aim of the study

This research was designed to achieve two principal goals. The primary objective was to synthesize a novel biosorbent from Norway Spruce Wood Residue, conduct its comprehensive characterization, and subsequently assess its performance as a viable adsorbent for eliminating specific heavy metal ions [Pb(II), Cd(II), Cu(II), and Zn(II)] from aqueous solutions. A second, parallel objective involved the synthesis and characterization of acid-modified sub-bituminous coal. The efficacy of this modified material was then evaluated for the purpose of removing ciprofloxacin (CFX), which was investigated as a representative example of a persistent pharmaceutical pollutant.

Furthermore, this thesis provides a preliminary assessment for the contamination level by Cadmium in a local landfill soil in Madaba, Jordan, and presents an evaluation of groundwater vulnerability by adopting a proposed sustainable environmental management approach based on green chemistry principles.

1.3. Study objectives

Based on the problem statement, the following objectives were identified:

1. To experimentally determine the chemical composition and physical characteristics of the Norway Spruce Wood Residue (NSWR) and sub-bituminous coal precursors.
2. To evaluate the efficacy of untreated NSWR as a sustainable, cost-effective biosorbent for sequestering four specific heavy metals (Cd, Cu, Pb, Zn) from a competitive multi-element aqueous environment.
3. To evaluate the economic and adsorption potential of using sub-bituminous coal modified with H_2SO_4 and HNO_3 to remove ciprofloxacin from industrial effluent.
4. To fully characterize the raw and modified adsorbents (NSWR, raw coal, and acid-modified coals) using a suite of analytical techniques (e.g., FTIR, SEM-EDS, XRD, BET).

5. To investigate the impact of various operational factors specifically pH, contact time, initial ion concentration, particle size, temperature, and adsorbent dosage to identify the optimal conditions for pollutant removal.
6. To investigate the adsorption kinetics, equilibrium isotherms, and thermodynamics for both pollutant-adsorbent systems to elucidate the underlying removal mechanisms.
7. To explore the efficiency of a synthesized nano-adsorbent from NSWR for the remediation of a real wastewater laundry sample collected from a laundry shop in Madaba, Jordan.
8. To evaluate the usefulness of applying Artificial Intelligence (AI) regression models for predicting adsorption performance and comparing their efficacy against traditional kinetic models.
9. To conduct an environmental site assessment of a landfill in Madaba, Jordan, by quantifying Cadmium (Cd) soil contamination and evaluating the potential risk to groundwater resources, subsequently proposing a management and remediation strategy for the site

2. MATERIAL AND METHODS

2.1. Materials

2.1.1. Adsorbent Precursors

Two precursor materials were utilized for adsorbent preparation in this study. The first, a sub-bituminous coal, was obtained from the El-Maghara mine in Sinai, Egypt, selected for its high carbon content (68.4 wt.%), inherent porosity, and local availability. The second precursor, Norway Spruce Wood Residue (NSWR) (*Picea abies* (L.) Karst), was sourced as a forestry byproduct from Gödöllő, Hungary. This lignocellulosic biomass was chosen due to its low cost, widespread availability, and natural affinity for binding heavy metal ions via its oxygen-containing functional groups.

2.1.2. Chemicals and Reagents

All experimental procedures were conducted using analytical-grade chemicals and reagents. The chemical modification of coal was performed using sulfuric acid (H_2SO_4, 98%) and nitric acid (HNO_3, 65%). The model pharmaceutical pollutant investigated was ciprofloxacin (CFX; $C_{17}H_{18}FN_3O_3$; ≥98% HPLC purity, Sigma-Aldrich). For heavy metal adsorption experiments, stock solutions (1000 mg/L) were prepared using lead nitrate ($Pb(NO_3)_2$), copper nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$), cadmium chloride hemi-pentahydrate ($CdCl_2 \cdot 2.5H_2O$), and zinc nitrate ($Zn(NO_3)_2$) from Merck (Germany). Sodium nitrate ($NaNO_3$) was used to maintain constant ionic strength, while sodium hydroxide (NaOH) was used for pH adjustment. All chromatographic analyses utilize HPLC-grade methanol. Ultrapure deionized water (ddH_2O), with a resistivity of 18.2 MΩ·cm produced by a Merck Milli-Q system, was used for all aqueous solution preparations and rinsing procedures.

2.2. Methods

2.2.1. Adsorbent Preparation

2.2.1.1. Acid-Modified Coal Synthesis

The synthesis of Sulfuric acid-modified Coal (S.C) and Nitric acid-modified Coal (N.C) followed a standardized two-step chemical oxidation protocol. Raw sub-bituminous coal was first ground to a particle size range of 20-70 µm to maximize effective surface area. For the acid modification, 10-gram portions of the ground coal were dispersed separately into 100 mL of 95% H_2SO_4 and 50 mL of 65% HNO_3. The mixtures were homogenized and heated to 150°C for a controlled reaction time of 60 minutes. Following treatment, the modified coal samples were rigorously washed with ddH_2O until the supernatant reached a neutral pH (≈7), confirming complete removal of free acid. The washed samples were then dried at 65°C for 10 hours and stored in sealed containers.

2.2.1.2. Biomass Processing and Nanocrystal Synthesis

The raw *Picea abies* sample underwent an initial purification step of thorough rinsing with ddH_2O to remove any adhering soil or debris. The rinsed biomass was then dried in an oven at 85°C for 48 hours to ensure complete moisture removal and inhibit microbial activity. Post-drying, the specimen was ground into a fine powder and sieved to isolate a precise particle size fraction between 90 and 250 µm. The prepared NSWR biomass powder was stored in a desiccator.

To synthesize nanocrystals (Nano-NSWR), the NSWR powder was processed via a modified acid hydrolysis procedure. 5.0 g of the sieved biomass was dispersed in 50 mL of 64 wt.% H_2SO_4 under constant stirring at 45°C for 2 hours. The reaction was terminated by adding ice-cold deionized water. The resulting suspension was subjected to repeated cycles of centrifugation (10,000 rpm for 15 minutes) and re-dispersion in ddH_2O until the supernatant reached neutral pH. The suspension was then dialyzed against deionized water for 48 hours to remove residual impurities, followed by ultrasonication to ensure a uniform dispersion. Finally, the nanocrystal suspension was freeze-dried to yield a dry powder.

2.2.2. Adsorbent Characterization Techniques

A suite of complementary techniques was applied to characterize the physicochemical properties of the prepared adsorbents.

- **X-Ray Diffraction (XRD) Analysis:** The crystalline structure and phase composition were determined using a PANalytical Empyrean X-ray diffractometer with Cu-Kα radiation over a 2θ angular range of 5° to 80°.
- **Fourier Transform Infrared Spectroscopy (FTIR):** Surface chemistry and functional groups were identified using an FTIR spectrometer over a spectral range of 4000 to 400 cm^{-1}. Coal-based samples were prepared as KBr pellets.
- **Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS):** Surface morphology and elemental composition were examined using a Gemini Zeiss-Ultra 55 scanning electron microscopes with an integrated EDS system.

- **Surface Area and Porosity Analysis:** The textural properties were quantified by measuring nitrogen (N_2) adsorption-desorption isotherms at 77 K. Specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method, while pore volume and size distribution were determined using the Barrett-Joyner-Halenda (BJH) method.
- **Determination of Point of Zero Charge (pH_{PZC}):** The pH at which the adsorbent's net surface charge is zero was determined using the pH drift method.

2.2.3. Batch Adsorption Experiments

- **Ciprofloxacin (CFX) Removal using Coal-Based Adsorbents:** Experiments were conducted to assess the efficacy of raw (R.C), sulfuric acid-modified (S.C), and nitric acid-modified (N.C) coal. A fixed adsorbent dosage of 0.2 g/L was used in a 250 mL solution volume. Key operational parameters investigated were solution pH (range 2 to 9), contact time (30 to 1200 minutes), and initial CFX concentration (100 to 800 mg/L).
- **Heavy Metal Removal using Picea abies Biomass (NSWR):** Experiments were performed for the simultaneous removal of Pb(II), Cu(II), Zn(II), and Cd(II) ions from a quaternary aqueous solution. The standard procedure involved agitating a defined quantity of NSWR in 50 mL of the metal solution at 200 rpm in a temperature-controlled shaker. The following parameters were systematically varied: pH (2.0 to 6.0), mixing time (up to 400 mins), particle size (<90 µm to 1000 µm), temperature (25°C to 45°C), adsorbent mass (0 to 0.5 g), and stirring speed (40 to 400 rpm).
- **Adsorption from Real Laundry Wastewater:** Nanocellulose synthesized from NSWR was used as an adsorbent for the treatment of potential heavy metals in real wastewater effluents obtained from a local laundry shop in Madaba, Jordan.

2.2.4. Analytical Methods and Data Analysis

- **Pollutant Quantification:** Ciprofloxacin (CFX) concentration was quantified using a High-Performance Liquid Chromatography (HPLC) system equipped with a UV detector. Residual heavy metal ion concentrations were quantified using an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES).
- **Data Modeling:** The experimental adsorption capacity at equilibrium (Qe) and removal efficiency (R%) were calculated. The data were fitted to several kinetic models (Pseudo-First-Order, Pseudo-Second-Order, Weber-Morris Intraparticle Diffusion) and isotherm models

(Langmuir, Freundlich, Dubinin-Radushkevich, Temkin) via non-linear regression to elucidate adsorption mechanisms. Thermodynamic parameters ($\Delta G°$, $\Delta H°$, and $\Delta S°$) were calculated from the temperature dependence of the equilibrium constant.

- **Predictive Model Evaluation:** A computational workflow was executed to evaluate six regression models (Linear Regression, Decision Tree, Random Forest, SVR, Gradient Boosting, and XGBoost) for predicting adsorption capacity. Performance was quantified using Mean Absolute Error (MAE), Root Mean Squared Error (RMSE), and the coefficient of determination (R^2).

3. RESULTS AND DISCUSSION

This chapter provides a detailed presentation and interpretation of the experimental findings. The results are systematically organized into two primary parts, beginning with the investigation of acid-modified coal for ciprofloxacin removal, followed by the study of Norway Spruce Wood Residue for heavy metal sequestration.

3.1. Acid-Modified Coal for Ciprofloxacin Removal (Al-Labadi et al., 2023)

3.1.1. Characterization of Acid-Modified Coal

The structural, chemical, and morphological characteristics of the raw coal, alongside its acid-modified counterparts, were examined using a suite of analytical techniques. The primary objective of these analyses was to elucidate the transformations in the coal's crystalline structure, surface functional groups, and topography resulting from the acid modification, as these properties fundamentally govern its adsorptive performance.

3.1.1.1. XRD Analysis

The structural modifications induced by acid treatment were investigated by comparing the X-ray diffraction (XRD) patterns of the raw coal (RC) with those of the sulfuric acid-modified (SC) and nitric acid-modified (NC) samples, as depicted in **Figure 1**. The diffractogram for the untreated raw coal (**Figure 1A**) shows broad peaks, which confirms the amorphous nature of the precursor material prior to modification. Following treatment with H_2SO_4, the resulting SC sample (**Figure 1B**) exhibited a substantial alteration in its diffraction pattern, including a significant shift in the first peak (10°–32°) and a marked decrease in the intensity of the second peak. These changes are indicative of considerable disruption to the C-O-C linkages within the coal structure, a consequence of the oxidation process that enhances the material's amorphous character through dehydration into a polyaromatic carbon structure. A similar, though less pronounced, trend was observed for the NC sample (**Figure 1C**), where the primary peaks showed slight shifts and reductions in intensity relative to the raw coal, but not to the extent seen with the SC sample. Collectively, these XRD findings suggest that sulfuric acid treatment imparts a more profound oxidation and dehydration effect on the coal's structure, leading to a greater degree of amorphization compared to the nitric acid modification.

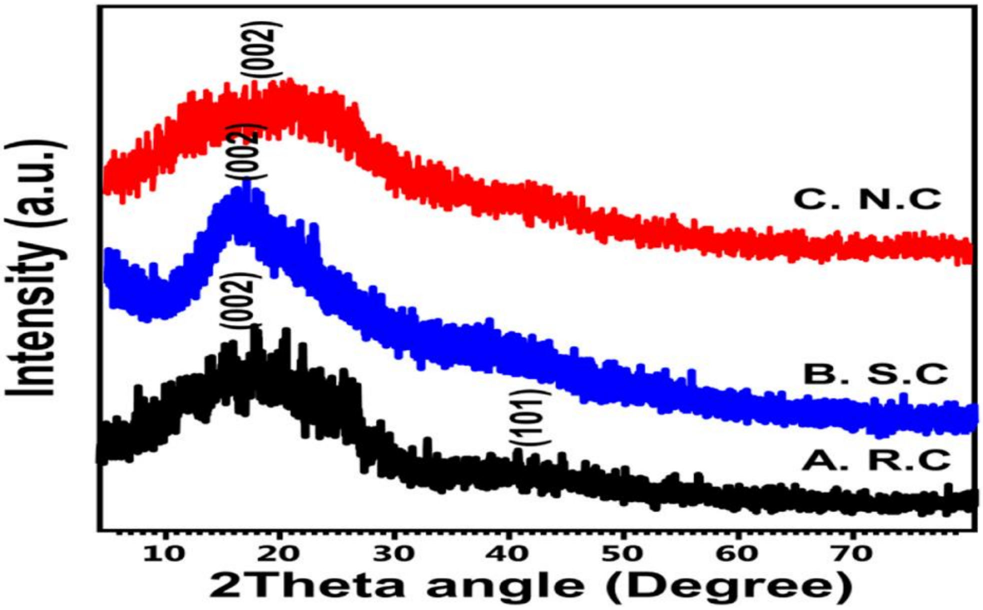

Figure 1. Comparative XRD diffractograms of (A) the raw coal (RC) precursor, (B) the sulfuric acid-treated coal (SC), and (C) the nitric acid-treated coal (NC)**.**

3.1.1.2. FTIR Analysis

Fourier Transform Infrared (FTIR) spectroscopy was employed to identify the changes in surface functional groups resulting from the acid treatments. The FTIR spectrum of the raw coal precursor (**Figure 2A**) exhibited characteristic absorption bands, including those for aromatic C-H (500–900 cm^{-1}), aliphatic C-H (2858–2940 cm^{-1}), C-O stretching (1000–1200 cm^{-1}), aromatic C=C (1616 cm^{-1}), carbonyl C=O (1716 cm^{-1}), and a broad -OH band (3000–3600 cm^{-1}) (Boral et al., 2021).

Significant alterations were observed in the spectra of the modified samples. For the sulfuric acid-treated coal (SC), the spectrum (**Figure 2B**) showed a notable intensification of the hydroxyl band (~3398 cm^{-1}) and the C=O band (~1712 cm^{-1}), confirming a strong oxidative effect and the introduction of carboxylic acid groups (–COOH) (Mateo et al., 2021). Furthermore, new bands appeared that are characteristic of sulfur-containing functional groups, including $-SO_3H$ (1133 cm^{-1}), O=S=O (1025 cm^{-1} and 1001 cm^{-1}), and C-S (578 cm^{-1}) (Mateo et al., 2021). Similarly, the nitric acid-treated coal (NC) spectrum (**Figure 2C**) displayed a pronounced shift in the -OH band (~3355 cm^{-1}) and an enhancement of the C=O stretching band (~1716 cm^{-1}). Critically, this sample also showed new absorption bands assigned to nitrogen-containing groups, such as N=O and C-N stretching (~1546 cm^{-1}), which confirms the incorporation of new active sites via nitric acid oxidation (Alvarez et al., 2003).

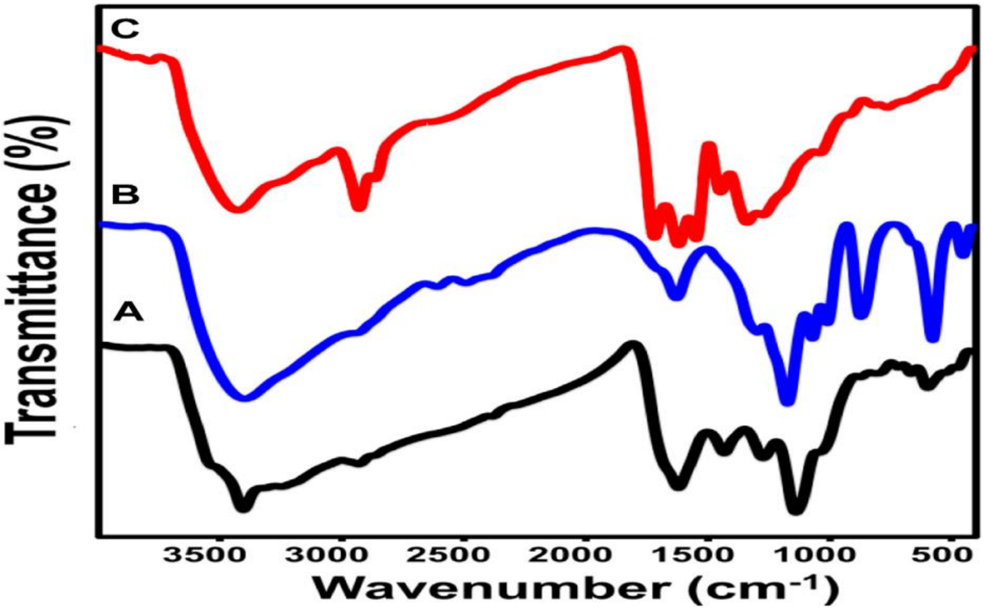

Figure 2. Comparative FTIR Spectra Illustrating the Chemical Structure of (A) Raw Coal (RC), (B) Sulfuric Acid-Treated Coal (SC), and (C) Nitric Acid-Treated Coal (NC).

3.1.1.3. Morphological and Textural Analysis

The FTIR analysis was corroborated by elemental analysis, which quantified the changes in the materials' chemical composition (**Table 1**). The data reveal a substantial increase in the nitrogen (N) content for the N.C sample and the sulfur (S) content for the S.C sample, confirming the successful incorporation of new, element-specific functional groups. The significant increase in sulfur content within the S.C material is attributed to sulfonation reactions, where sulfuric acid's interaction with the coal structure leads to the formation of effective electrophiles (Yu et al., 2018). Similarly, the elevated nitrogen content in the N.C sample is a result of electrophilic nitration, where the nitrenium ion (NO_2^+) acts as the primary electrophile, attacking the aromatic rings to form nitrobenzene-type compounds on the coal surface (Shi et al., 2012).

Table 31. Chemical Composition, Acid Density, and Surface Area Properties of Raw Coal (R.C), Sulfuric Acid-Modified Coal (S.C), and Nitric Acid-Modified Coal (N.C) Adsorbents.

Parameter	**R.C**	**N.C**	**S.C**
C (Wt. %)	68.4	53.2	48.8
S (Wt. %)	2.32	2.12	7.6
N (Wt. %)	2.53	9.3	7.6
H (Wt. %)	6.3	8.72	10.8
O (Wt. %)	10.6	19.7	24.4
Acid density (mmol/g)	0.064	4.62	8.4
Surface area (m^2/g)	5.4	18.3	26.4

Scanning Electron Microscopy (SEM) was used to visualize the morphological changes induced by the acid treatments (**Figure 3**). The untreated raw coal (**Figure 3A**) presented a relatively smooth and compact surface. In stark contrast, the sulfuric acid-treated coal (SC) displayed a markedly more rugged and irregular topography, featuring numerous nanoscale protrusions and the formation of new micropores (**Figures 3B, C**). These features are likely a result of the acid leaching mineral impurities from the coal matrix. The nitric acid-treated sample (NC), while also showing evidence of surface modification, did not exhibit the same degree of topographical alteration (**Figure 3D**). These visual changes corresponded directly with significant alterations in the material's textural properties, as quantified by surface area and porosity analysis (**Table 1**). A substantial enhancement in the specific surface area was observed, increasing from 5.4 m²/g in the raw coal to 18.3 m²/g for NC and 26.4 m²/g for SC. This was accompanied by a dramatic increase in the total pore volume, which rose from 0.011 cm³/g for the raw material to 0.41 cm³/g and 0.48 cm³/g for NC and SC, respectively.

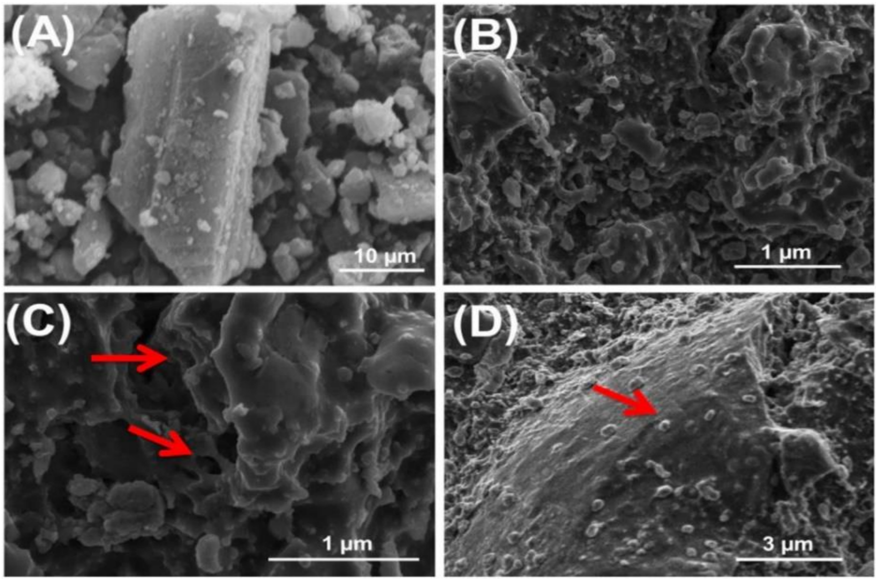

Figure 3. SEM micrographs illustrating the surface morphology of: (A) raw coal (RC); (B, C) sulfuric acid-treated coal (SC) at different magnifications; and (D) nitric acid-treated coal (NC).

3.1.2. Adsorption of CFX molecules

3.1.2.1. Effect of Solution pH

The influence of solution pH on the adsorption of Ciprofloxacin (CFX) was investigated over a pH range of 2 to 9. Solution pH is a critical variable as it governs both the surface charge of the adsorbent and the speciation of the CFX molecule. The results show that the CFX uptake capacity for all three adsorbents increased progressively with rising pH, reaching maximum values at approximately pH 8 (**Figure 2A**). This behavior can be explained by the interplay between the adsorbent surface charge and the zwitterionic nature of CFX, which has two dissociation constants ($pKa_1 = 6.1$ and $pKa_2 = 8.7$) (Gor & Dave, 2020). At highly acidic conditions ($pH < pH_{PZC}$), the adsorbent surfaces are positively charged, leading to electrostatic repulsion with the cationic CFX^+. Conversely, at highly alkaline conditions ($pH > 9$), both the adsorbent surfaces and the CFX molecules are negatively charged, again resulting in repulsion. The optimal adsorption observed in the pH 6-8 range is therefore attributed to favorable electrostatic interactions between the negatively charged surfaces of the adsorbents (as the pH is above their respective pH_{PZC} values) and the zwitterionic and cationic forms of the CFX molecules.

3.1.2.2. Kinetic Studies

To determine the time required to reach equilibrium and investigate the rate of adsorption, the uptake of CFX was monitored over a time course of 1080 minutes. The kinetic profiles for all three adsorbents are presented in **Figure 2B**, revealing a characteristic two-stage adsorption process. An initial, rapid uptake phase was observed, followed by a much slower secondary phase until a plateau was reached, indicating that the system had achieved equilibrium. At this point, the equilibrium adsorption capacities (Q_e) were determined to be 88.3 mg/g, 102.5 mg/g, and 127.8 mg/g for RC, NC, and SC, respectively. This kinetic behavior can be explained by the initial abundance of unoccupied, readily accessible active sites. As these sites become progressively occupied, the concentration gradient decreases, leading to a slower uptake rate (El-Sherbeeny et al., 2021).

The Weber-Morris intra-particle diffusion model was applied to the kinetic data (**Figure 2C**). The multi-linear nature of these plots, which do not pass through the origin, indicates that the overall adsorption process is not governed by a single mechanism but is instead a multi-stage process influenced by more than one rate-limiting step, including external surface adsorption and intra-particle diffusion (El Qada, 2020).

The experimental kinetic data were fitted to the non-linear forms of the Pseudo-First Order (PFO) and Pseudo-Second Order (PSO) models (**Figures 2D, E, F**). The goodness-of-fit was quantitatively evaluated by comparing the coefficient of determination (R^2) and Chi-squared (χ^2) values for each model (**Table 2)**. The results of the non-linear regression analysis indicate that the PFO model provides a superior fit to the experimental data for all three adsorbents. The strong fit of the PFO model suggests that the adsorption process is predominantly governed by physisorption mechanisms, such as electrostatic attraction (Sherlala et al., 2019). Nevertheless, the data also shows a reasonably strong fit to the PSO model, implying that the overall adsorption mechanism is likely a complex interplay of mechanisms, where physically adsorbed CFX molecules may form layers on top of a base layer that is more strongly bound via chemisorption (Jasper et al., 2020).

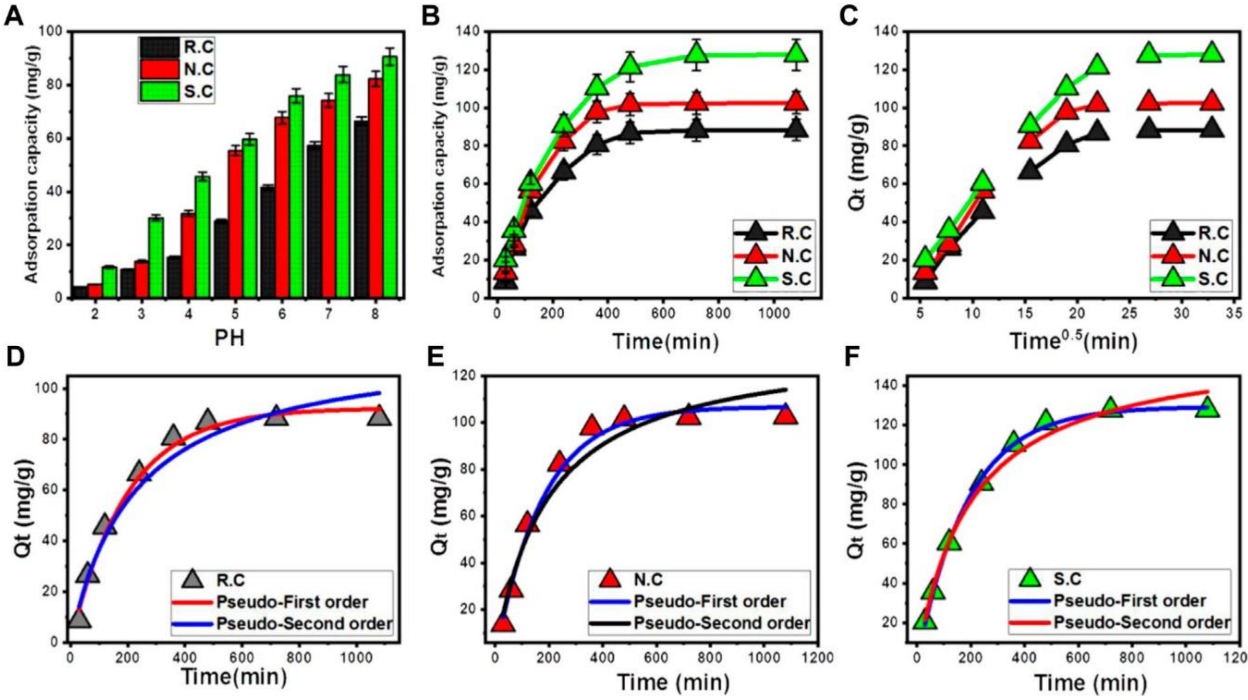

Figure 4. Adsorption of CFX onto coal-based adsorbents. (A) Effect of solution pH; (B) Effect of contact time; (C) Intra-particle diffusion model plots. Non-linear kinetic model fitting for (D) RC, (E) NC, and (F) SC.

Table 2. Comparison of Parameters Derived from Pseudo-First Order and Pseudo-Second-Order Kinetic Models for CFX Adsorption.

Model	**Parameter**	**Unit**	**Raw Coal (RC)**	**Nitric Acid Coal (NC)**	**Sulfuric Acid Coal (SC)**
Pseudo-First Order	k_1	min^{-1}	0.005	0.0056	0.0053
	Q_e,calc	mg/g	92.25	106.70	129.34
	R^2	-	0.98	0.99	0.99
	χ^2	-	0.50	0.28	0.037
Pseudo-Second Order	k_2	g/mg·min	3.77×10^{-5}	3.85×10^{-5}	3.12×10^{-5}
	Q_e,calc	mg/g	118.50	134.37	161.99
	R^2	-	0.96	0.96	0.99
	χ^2	-	1.05	0.97	0.25

3.1.3. Isotherm and Thermodynamic Studies

3.1.3.1. Effect of Initial CFX Concentration and Temperature

To determine the maximum adsorption capacity (Q_{max}) and to investigate the equilibrium behavior, isotherm experiments were conducted by varying the initial CFX concentration from 100 to 800 mg/L at three different temperatures (298 K, 308 K, and 318 K). As shown in **Figures 5A** to **5C**, the equilibrium adsorption capacity of all three materials increased with higher initial CFX concentrations. This phenomenon is attributed to the enhanced concentration gradient, which provides a greater driving force for mass transfer (Ashraf et al., 2022). For each adsorbent, the uptake capacity eventually reached a plateau, signifying surface saturation. The acid modification significantly enhanced the adsorption performance of the coal. Furthermore, for all three adsorbents, the Q_{max} values consistently increased with rising temperature, indicating that the CFX adsorption process is endothermic in nature.

3.1.3.2. Application of Isotherm Models

To describe the equilibrium behavior, the experimental data were fitted to the non-linear forms of three widely recognized isotherm models: Langmuir, Freundlich, and Dubinin–Radushkevich (D-R). The graphical fits for each model are presented in **Figures 5D** through **5L**. The results clearly indicate that the Langmuir model provides a superior fit for all three adsorbents across all tested temperatures. The strong applicability of the Langmuir model suggests that the adsorption of CFX primarily occurs as a monolayer onto a finite number of energetically homogeneous active sites on the adsorbent surfaces (Abukhadra et al., 2022; Assayed et al., 2022). The mean free energy of adsorption (E) calculated from the D-R model was consistently below 8 kJ/mol, which strongly supports the conclusion that the dominant mechanism is physisorption (Dawodu et al., 2012).

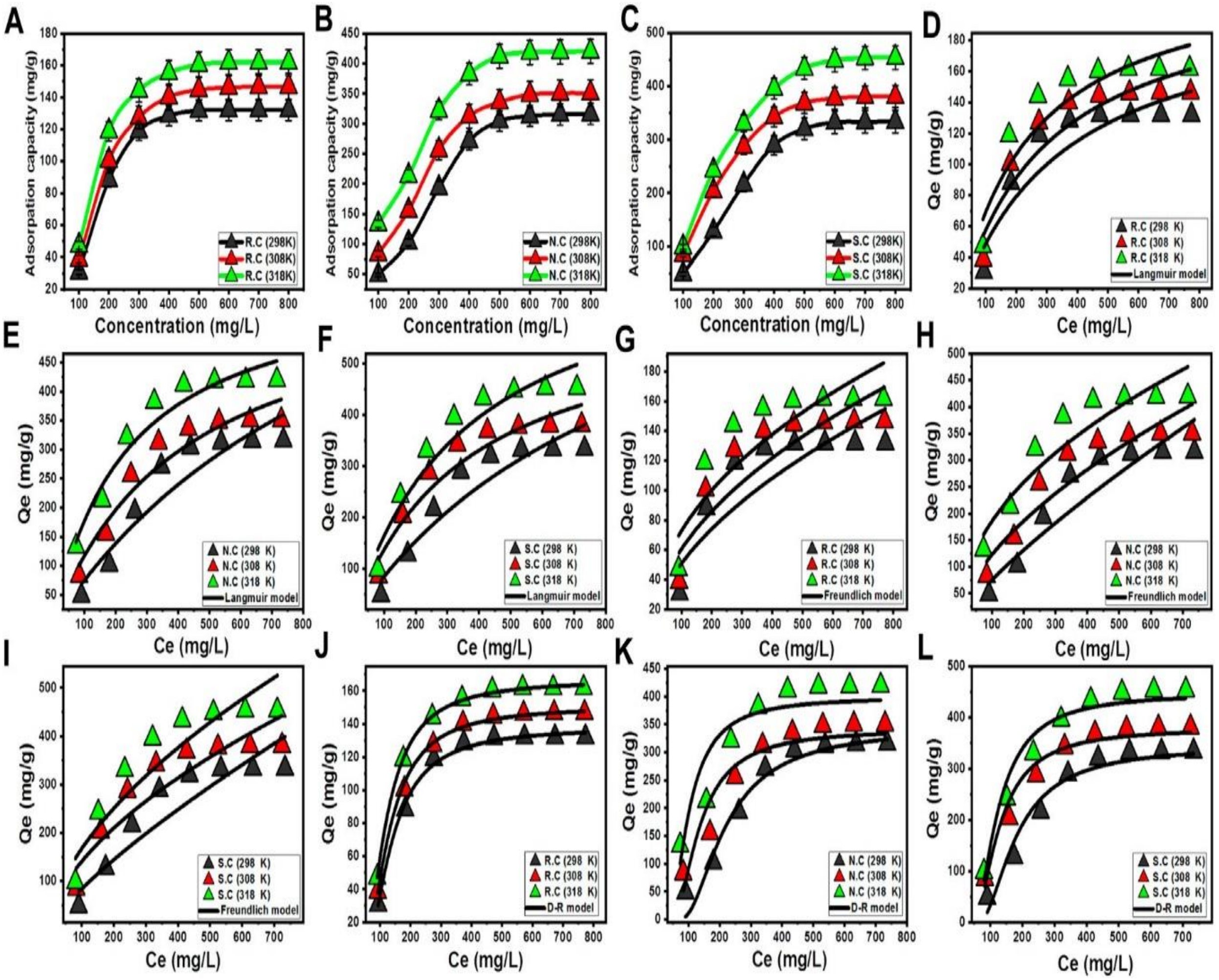

Figure 5. Isotherm analysis of CFX adsorption. (A-C) Effect of initial concentration at different temperatures. Non-linear isotherm model fits for (D-F) Langmuir, (G-I) Freundlich, and (J-L) Dubinin-Radushkevich models.

4.1.5. Adsorbent Recyclability

The potential for practical application of the coal-based adsorbents was evaluated by conducting five consecutive adsorption-desorption cycles. The results are presented in **Figure 6**. All three materials demonstrated significant stability and retained a high percentage of their initial adsorption capacity. For the sulfuric acid-modified coal (SC), the most effective adsorbent, the CFX uptake capacity decreased only slightly, from an initial 453.5 mg/g in the first run to 415.2 mg/g in the fifth run. The gradual decline in performance can be attributed to minor loss of adsorbent mass during washing and the irreversible blocking of some active sites by strongly bound CFX molecules.

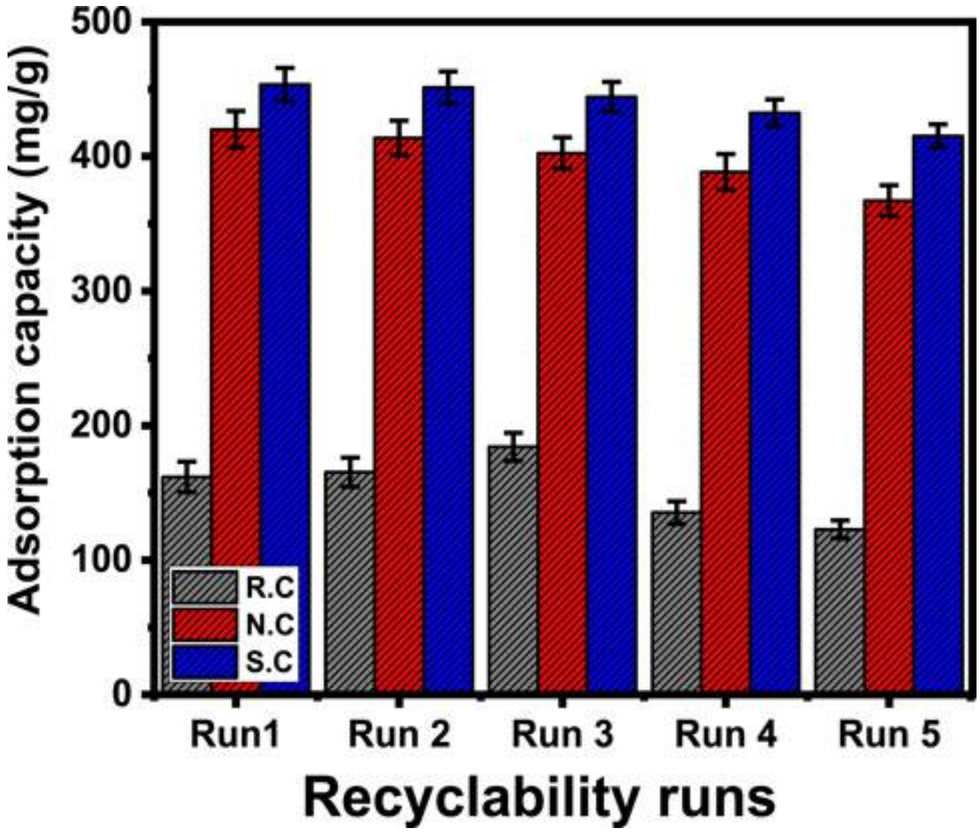

Figure 6. Performance of Raw Coal (RC), Nitric Acid-Modified Coal (NC), and Sulfuric Acid-Modified Coal (SC) over five consecutive cycles of CFX adsorption and regeneration.

3.1.6. Proposed Adsorption Mechanism

Based on the comprehensive material characterization and the results of the equilibrium studies, a multi-faceted adsorption mechanism is proposed to explain the uptake of Ciprofloxacin (CFX) onto the surfaces of the acid-modified coal adsorbents, as illustrated in **Figure 7**. The primary mechanisms are identified as:

- **Electrostatic Attraction:** The deprotonated acidic functional groups on the adsorbent surface (e.g., carboxyl $-COO^-$ and sulfonate $-SO_3^-$) are negatively charged at the optimal pH and exert a strong electrostatic attraction on the positively charged moieties of the CFX molecule.
- **Hydrogen Bonding:** The surfaces of the modified coals are rich in hydrogen-bond donor groups (e.g., –OH, –COOH) which can form strong hydrogen bonds with the numerous hydrogen-bond acceptor atoms (specifically nitrogen and oxygen) present in the chemical structure of the CFX molecule.

- ***π–π* Stacking Interactions:** The extensive network of aromatic rings within the coal's graphitic structure provides an electron-rich surface, which can interact with the aromatic rings of the CFX molecule through non-covalent π–π stacking.

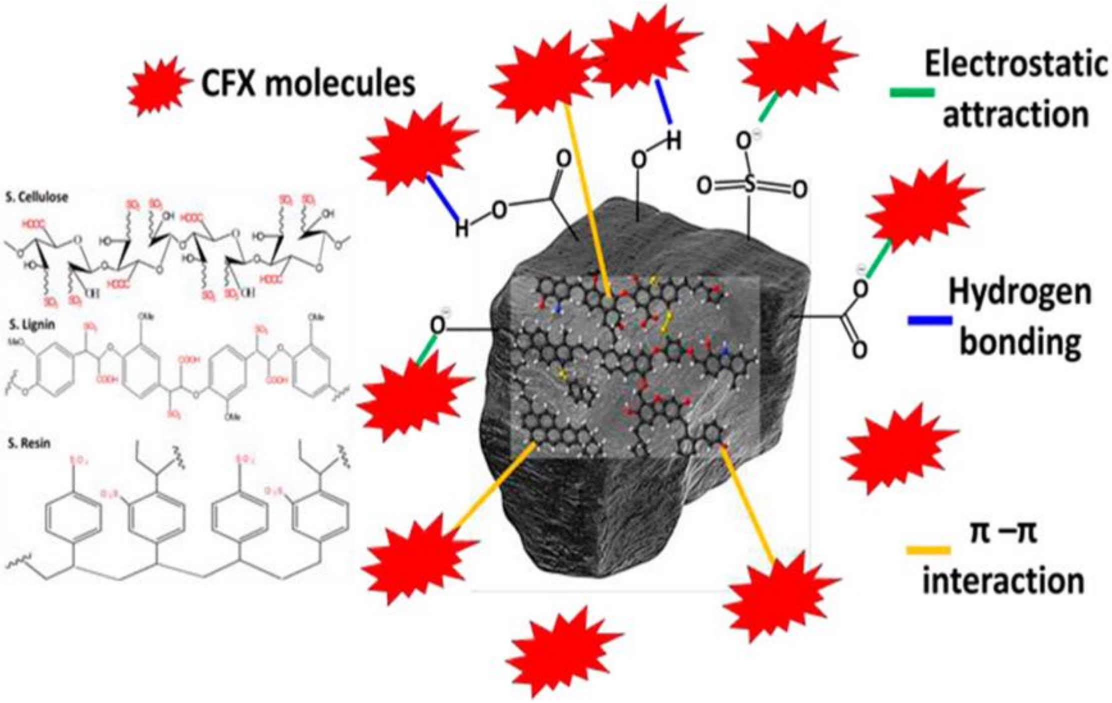

Figure 7. Proposed multi-modal mechanism for the adsorption of Ciprofloxacin (CFX) onto the surface of modified coal, illustrating the key roles of electrostatic attraction, hydrogen bonding, and π–π interactions.

3.2. Picea abies Biomass for Heavy Metal Removal

3.2.1. Biosorbent Characterization

The physicochemical characteristics of the Norway Spruce Wood Residue (NSWR) were analyzed to establish its baseline properties. The composition is typical of a lignocellulosic material (Bhardwaj et al., 2025; Meshitsuka & Isogai, 2017). FTIR spectroscopy confirmed the material's lignocellulosic nature, with a prominent, broad absorption band at approximately 3330 cm^{-1} attributed to O-H stretching vibrations of hydroxyl groups present in cellulose, lignin, and adsorbed water (**Figure 8**). Collectively, the presence of this diverse array of oxygen-containing functional groups indicates that the NSWR surface possesses numerous potential active sites for heavy metal sequestration.

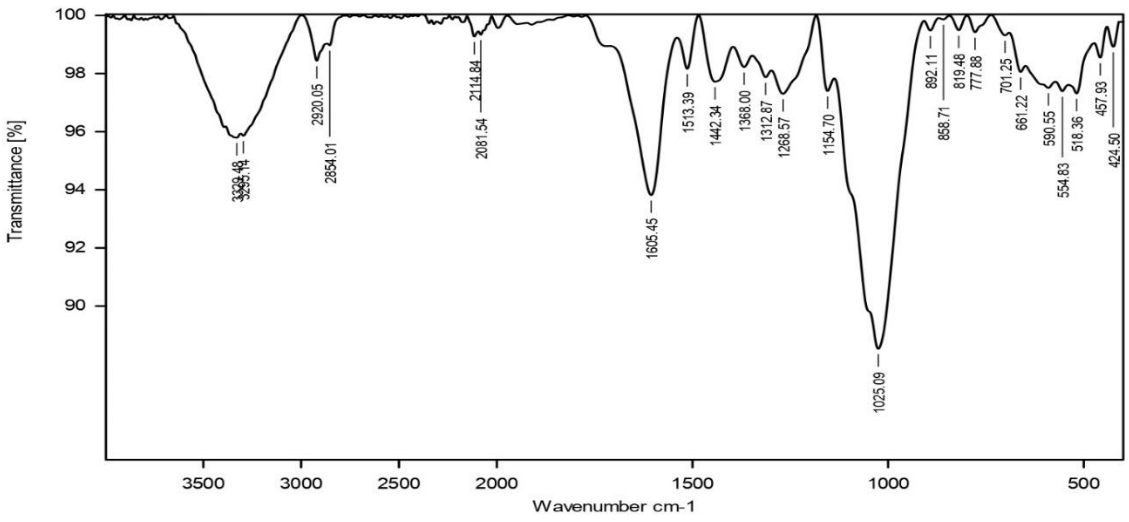

Figure 8. FTIR spectrum of the NSWR biomass, identifying key surface functional groups.

X-ray diffraction (XRD) pattern of the unmodified NSWR biomass confirmed the predominantly amorphous or poorly crystalline nature of lignocellulosic materials (**Figure 9**). The surface topography was visualized using SEM, revealing a highly heterogeneous and irregular surface. After the adsorption process, Energy-Dispersive X-ray Spectroscopy (EDS) confirmed the successful uptake of all four target heavy metals, as evidenced by the distinct characteristic peaks for Lead (Pb), Copper (Cu), Cadmium (Cd), and Zinc (Zn) (**Figure 9**). A high abundance of Calcium (approx. 16 wt%) was also detected, along with smaller amounts of other inherent elements. The significant presence of these inherent cations, particularly Ca^{2+}, strongly suggests that ion exchange is a key contributing mechanism to the overall heavy metal adsorption process (Marin & Ayele, 2002).

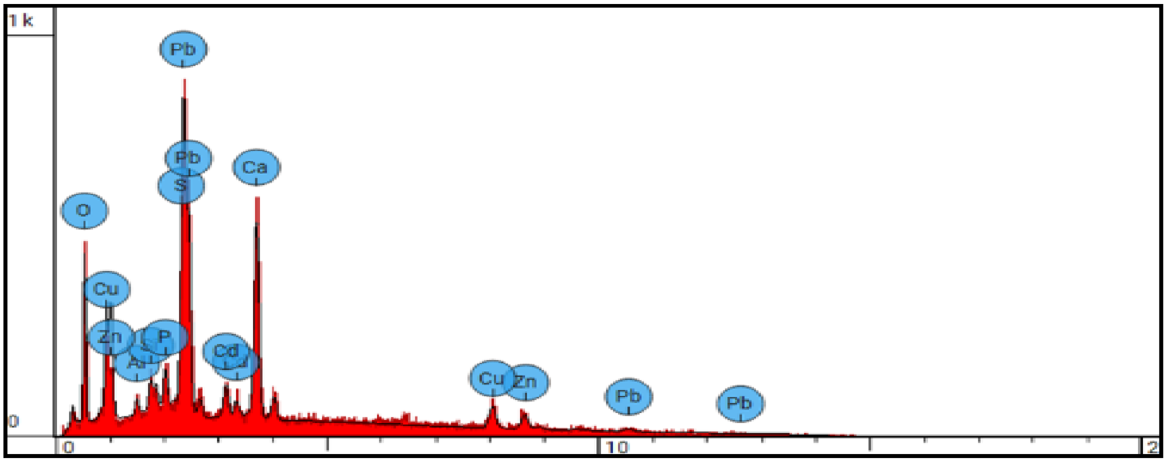

Figure 9. Energy-Dispersive X-ray Spectrum of the NSWR biomass following the adsorption of the quaternary heavy metal solution.

The point of zero charge (pH_{PZC}) of the NSWR biosorbents was determined to be 5.7, as illustrated in **Figure 10**. The pH_{PZC} represents the pH at which the net charge on the adsorbent's surface is neutral. Consequently, at pH values greater than 5.7, the NSWR surface will carry a net negative charge, creating favorable conditions for the electrostatic attraction of positively charged heavy metal cations (Al-Labadi et al., 2025).

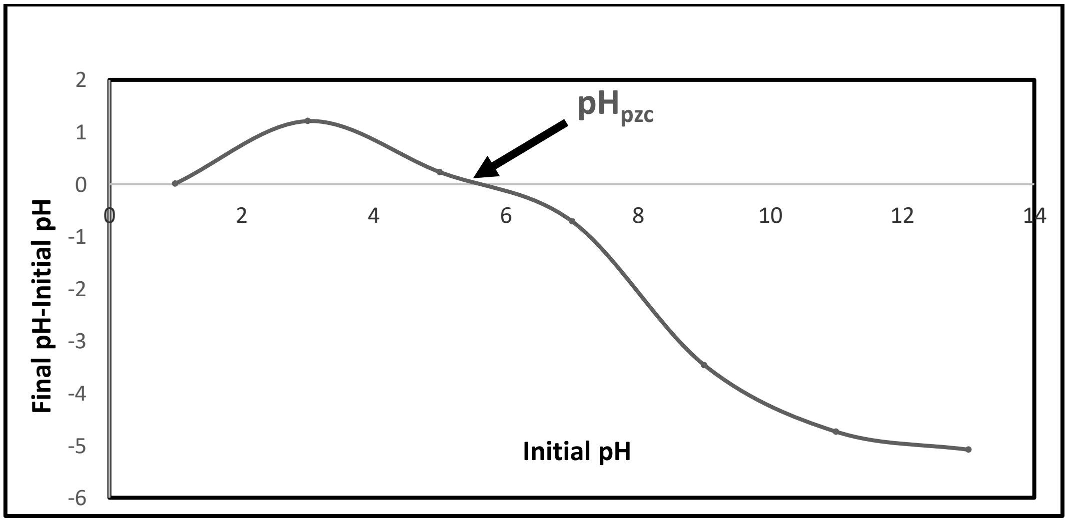

Figure 10. Determination of the point of zero charge (pH $_{PZC}$) for the NSWR biosorbent using the pH drift method.

3.2.2. Parametric Studies

The effect of biosorbent dosage on removal efficiency was investigated from 0.005 g to 0.1 g. The results (**Figure 11**) demonstrate a direct positive correlation between dosage and removal efficiency for all four metal ions, attributed to the increased availability of total active binding sites. A dosage of 0.1 g in 10 mL (10 g/L) was selected as optimal.

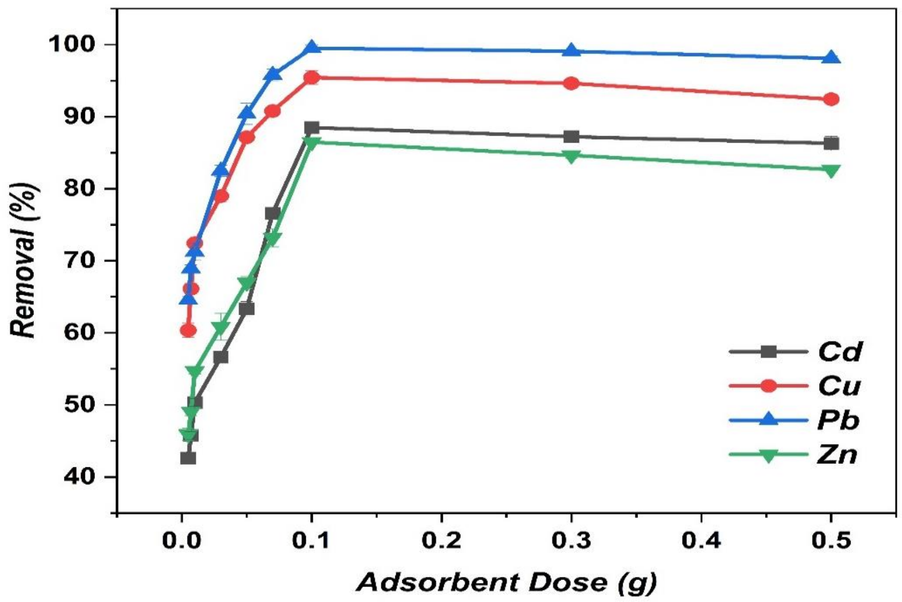

Figure 11. Influence of NSWR dosage on the removal efficiency (%) of Cd (II), Cu (II), Pb (II), and Zn (II).

The effect of contact time was investigated to determine the equilibrium time (**Figure 12**). The adsorption process was characterized by an initial, rapid uptake phase, with equilibrium reached for all four metals by approximately 200 minutes. The effect of pH was investigated over a range from 2 to 6 (**Figure 13**). The optimal pH range for adsorption was identified as 5 to 6, which aligns with previous studies on cellulosic materials (Bhattacharjee et al., 2020) and avoids potential precipitation of metal hydroxides.

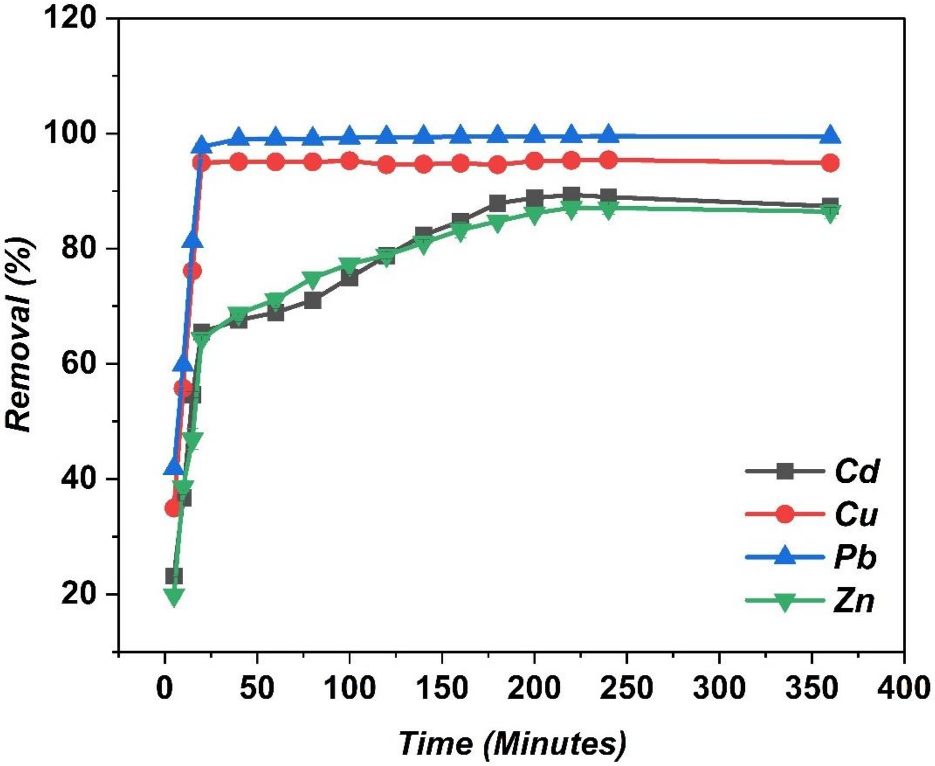

Figure 12. Effect of contact time on the removal efficiency (%) of Pb(II), Cu(II), Zn(II), and Cd(II) by the NSWR biosorbent.

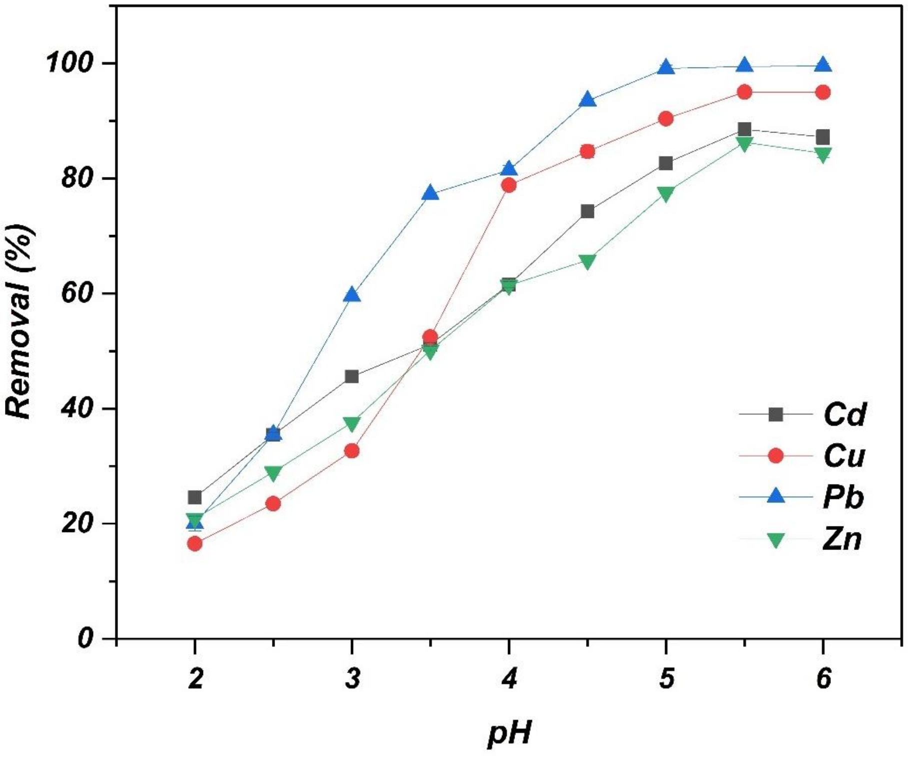

Figure. 13. The effect of solution pH on the removal efficiency (%) of Pb(II), Cu(II), Zn(II), and Cd(II) by the NSWR biosorbent.

3.3. Competitive Adsorption and Selectivity

To evaluate the performance of NSWR in a multi-component system, competitive adsorption experiments were conducted. The results (**Figure 14**) demonstrate a clear selectivity sequence: Pb(II) > Cu(II) > Cd(II) > Zn(II). Pb(II) was preferentially adsorbed with the highest uptake capacity, a finding consistent with literature for various biosorbents (Amar et al., 2021). This observed selectivity correlates with the intrinsic physicochemical properties of the metal ions, particularly electronegativity and covalent index, suggesting the adsorption mechanism involves more than simple electrostatic attraction (Batool et al., 2018).

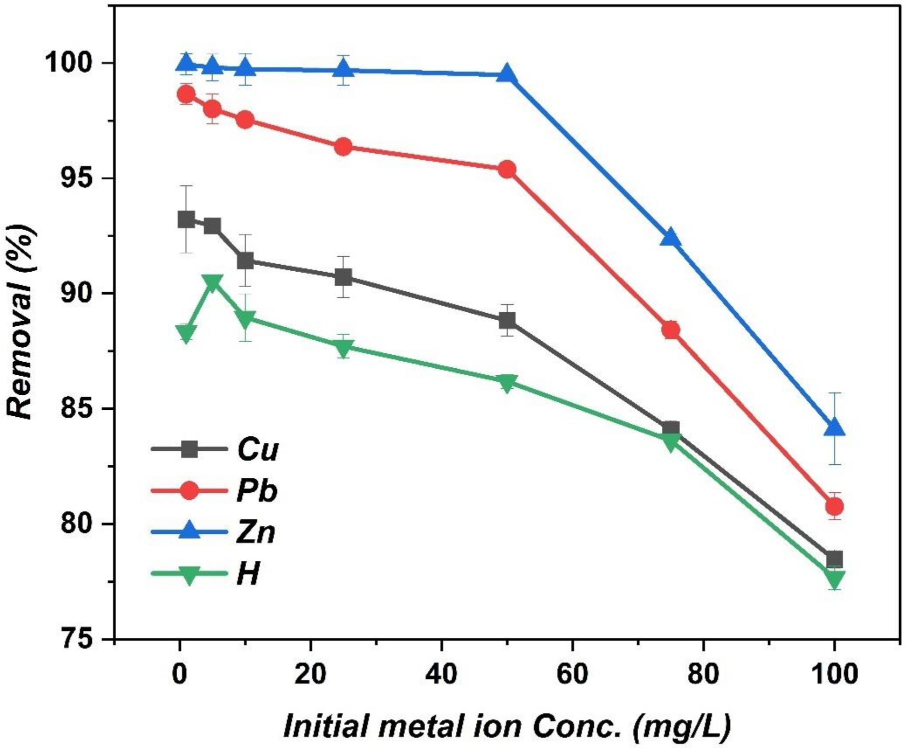

Figure 14. Competitive adsorption of Cd(II), Cu(II), Pb(II), and Zn(II) onto the NSWR biosorbent from a quaternary solution as a function of initial metal concentration..

3.4. Analysis of Adsorption Kinetics and Isotherms

Kinetic analysis revealed that the adsorption process was best described by the Pseudo-Second-Order (PSO) model, which consistently yielded the highest R^2 values (**Table 3**). The strong fit to the PSO model suggests that the rate-limiting step is likely chemisorption (Vishan et al., 2019; Weyrich et al., 2023). A comparative analysis of isotherm models clearly indicates that the Langmuir model provides a superior description of the equilibrium data for all four metals ($R^2 > 0.99$) compared to the Freundlich model (**Table 4**). The strong adherence to the Langmuir isotherm suggests that adsorption occurs predominantly as a monolayer onto a finite number of energetically uniform active sites (Dawodu et al., 2012).

Table 3. Langmuir and Freundlich isotherm parameters for the biosorption of heavy metals onto NSWR.

Element	Model
Langmuir	
Cd^{2+}	q_m(mgg^{-1}) =6.277, K_L (Lmg^{-1}) =0.2298, R$_L$ =R^2≈%99
Pb^{2+}	q$_m$(mgg^{-1}) =*10.325*, K_L (Lmg^{-1}) =3.211, R$_L$=R^2≈*0.99*
Cu^{2+}	q$_m$(mgg^{-1}) = *7.853*, K_L (Lmg^{-1})=0.5785, R$_L$=R^2 ≈ *0.99*
Zn^{2+}	q$_m$(mgg^{-1}) =*6.029*, K_L (Lmg^{-1}) =0.1712, R$_L$=R^2 ≈*0.99*
Freundlich	
Cd^{2+}	K$_f$ (mgg^{-1}) =0.9312, 1/n (gL^{-1}) =0.635, R^2≈*0.91*
Pb^{2+}	K$_f$ (mgg^{-1})=2.3577, 1/n (gL^{-1})=0.55, R^2≈*0.96*
Cu^{2+}	K$_f$ (mgg^{-1})=1.2915, 1/n =0.576, R^2≈*0.94*
Zn^{2+}	K$_f$ (mgg^{-1})=0.8383, 1/n (gL^{-1})=0.675, R^2≈*0.9*

Table 3. Kinetic parameters of PFO and PSO kinetic models of the 4 HMs on NSWR

	Pseudo-first order (PFO)			**Pseudo-second order (PSO)**		
Metal ion	K$_1$ (minute^{-1})	q$_e$ (calculated) (mg/g)	R^2	K$_2$ [g/(mg·min)]	q$_e$ (calculated) (mg/g)	R^2
Cd	0.003343	2.817	0.8796	0.0140	4.6364	0.9969
Cu	0.006165	0.49	0.5655	0.0687	4.8314	0.9993
Pb	0.00699	0.711	0.7632	0.0717	5.0392	0.9996
Zn	0.002996	2.376	0.9478	0.0152	4.5473	0.9989

As previously described in the methods, the parameters for the PSO model were determined from the slope and intercept of the linearized plot of t/q_t versus t.

4.3.1. Isotherm Modelling and Enhanced Adsorption Capacity of Nano-NSWR

To quantitatively validate the superior performance of the nano-formulated biosorbent, equilibrium adsorption data for Nano-NSWR were analyzed. As presented in **Figure 5**, the nano-formulated biosorbent shows a significant improvement in removal for all metals. Analysis of the Langmuir isotherm model revealed a dramatic enhancement in adsorption performance compared to the original NSWR biosorbent. The theoretical maximum monolayer adsorption capacities (q_{max}) derived from the Langmuir model are summarized in **Table 5**. Specifically, the q_{max} for Nano-NSWR was substantially higher across all tested metals, with capacity increasing by 76% for Lead, 63% for copper, 89% for Cadmium, and 84% for Zinc. This profound improvement is primarily attributed to the increased surface-area-to-volume ratio inherent in nanomaterials.

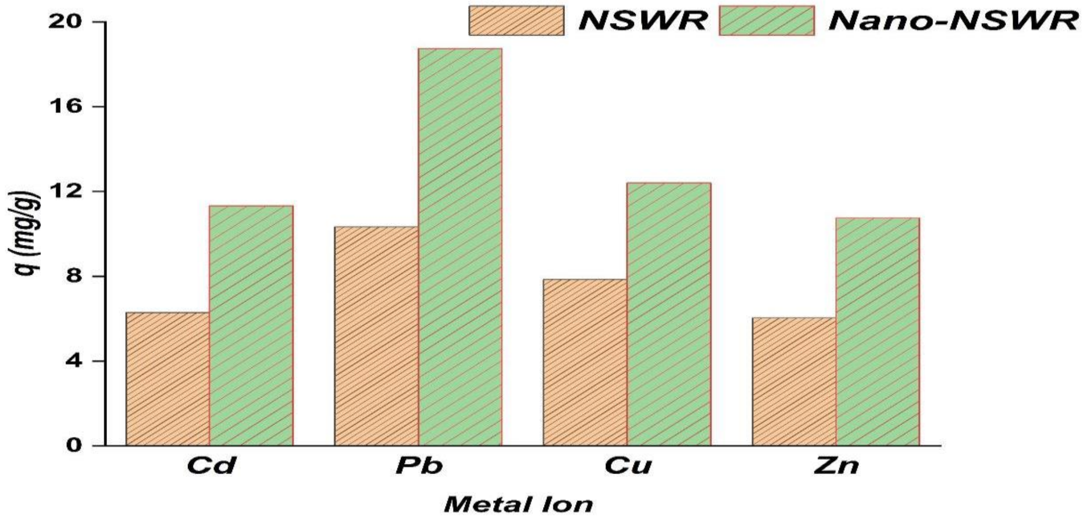

Figure 15. Comparison between NSWR and Nano-NSWR performance on (Cd, Pb, Cu, Zn) removal.

Table 5. Langmuir Isotherm Parameters for Heavy Metal Adsorption onto Nano-NSWR.

Metal Ion	Maximum Adsorption Capacity (q_{max}) (mg/g)	Coefficient of Determination (R^2)
Pb^{2+}	18.18	0.9782
Cu^{2+}	12.82	0.9998
Cd^{2+}	11.87	0.9891
Zn^{2+}	11.11	0.9934

4.3.2. Comparison between Performance on Synthesized and Real Wastewater

Several wastewater samples were collected from a commercial laundry shop in Madaba, Jordan (**Table 6**). The results of applying Nano-NSWR on these samples are shown in **Table 7**. The treatment was highly effective, achieving 100% removal for Pb and Cd, 91% for Cu, and 89% for Zn. These results demonstrate the high potential of Nano-NSWR for real-world applications.

Table 6. Average concentrations of PTEs obtained from laundry wastewater

TDS	pH	Temp.	Cd	Pb	Cu	Zn
1870	10.3	27 °C	0.031 mg/L	0.32 mg/L	1.2 mg/L	2.1 mg/L

Table 7. Average concentrations of PTEs obtained after treatment with nanocrystals from NSWR

	Cd	Pb	Cu	Zn
Treated water with nanocrystals (mg/L)	Not Detected	Not Detected	0.108	0.231
Removal efficiency %	100%	100%	91%	89%

3.4. Case Study: Cadmium Contamination at the Madaba Landfill

To establish the practical context for this research, an evaluation of Cadmium (Cd) contamination was conducted at the Madaba landfill site. The reliance on uncontrolled landfills is a significant environmental issue in Jordan. Analysis of soil samples collected from the site revealed Cd concentrations ranging from 3 to 24 µg/g. These values significantly exceed the maximum permissible limits set by Dutch and FAO/WHO standards, respectively. This level of soil contamination indicates a significant risk to the underlying groundwater aquifer (Kubier et al., 2019). Based on these findings, the most direct application of this research involves the engineering of enhanced landfill liner systems. Utilizing low-cost, locally sourced adsorbent materials such as the NSWR biomass—could create a reactive barrier to capture Cd and prevent its migration into the subsurface.

4. CONCLUSION AND RECOMMENDATIONS

4.1. Conclusion

This dissertation embarked on a multifaceted investigation to evaluate the potential of novel adsorbent materials derived from readily available, low-cost resources specifically modified sub-bituminous coal and unmodified Norway Spruce Wood Residue (NSWR) biomass for addressing the escalating challenges of water pollution. The research framework encompassed adsorbent synthesis, detailed physicochemical characterization, systematic optimization of adsorption processes, and mechanistic elucidation through comprehensive modeling. The findings unequivocally demonstrate the promising potential of these materials, providing data-driven conclusions that advance the understanding of sustainable pollutant sequestration from both pharmaceutical and heavy metal sources.

The investigation into **Modified Coal for Ciprofloxacin (CFX) Removal** proved that acid modification, particularly with sulfuric acid, is a strategically effective approach to dramatically enhance the inherent adsorption capacity of sub-bituminous coal. Characterization data from FTIR and BET analyses confirmed the successful introduction of oxygen- and sulfur-containing functional groups and a concurrent, significant increase in surface area, which directly correlated with improved CFX uptake. Under optimized conditions (pH 8, 25°C), sulfuric acid-modified coal (S.C) exhibited a remarkably high maximum adsorption capacity (Q_{max}) of 854.2 mg/g. This represents a substantial increase compared to the raw coal precursor. The kinetic analysis unequivocally supports a pseudo-first-order model, indicating a rate-limiting step linked to surface adsorption phenomena. Isotherm studies, strongly favoring the Langmuir model ($R^2 > 0.99$), validated a monolayer adsorption mechanism onto a homogenous adsorbent surface. Furthermore, initial recyclability tests demonstrated that the sulfuric acid-modified coal retains over 70% of its initial CFX adsorption capacity after five regeneration cycles, suggesting a reasonable degree of operational longevity and potential for cost-effective reuse.

The study of **NSWR Biomass for Heavy Metal Remediation** established this readily available agricultural waste product as a versatile and effective biosorbent. Comprehensive batch adsorption studies using a quaternary heavy metal solution [Cd(II), Cu(II), Pb(II), Zn(II)] and subsequently validated with real laundry wastewater—demonstrated NSWR's capability for simultaneous, multi-metal removal. Parametric optimization revealed the critical influence of pH (optimal range 5-6) and contact time (equilibrium reached within 200 minutes) on adsorption efficiency. Under these conditions, NSWR consistently achieved high removal efficiencies, particularly for lead and copper. The kinetic modeling provided the best fit to pseudo-second-order models, suggesting chemisorption is a significant mechanism, which is likely coupled with ion exchange as evidenced by EDS analysis. Langmuir isotherm fitting ($R^2 > 0.99$) characterized the adsorption process as monolayer and homogenous, yielding a selectivity sequence of Pb(II) > Cu(II) > Cd(II) > Zn(II). Importantly, the performance of NSWR was shown to be comparable, and in some instances superior to other lignocellulosic biosorbents reported in the literature, emphasizing its competitiveness as a low-cost alternative. The nano-formulation of NSWR (Nano-NSWR) resulted in a dramatic enhancement of adsorption capacity for all metals (e.g., an 89% increase for Cadmium), underscoring the high potential of nano structuring for improving adsorbent performance.

4.2. Significance, Challenges, and Limitations

The findings of this dissertation offer compelling evidence for the practical utility of both modified coal and NSWR biomass as cost-effective and sustainable adsorbents. The significant enhancement of CFX adsorption via acid modification presents a viable strategy for mitigating pharmaceutical contamination, while the efficacy of unmodified NSWR biomass positions this waste stream as a valuable resource for heavy metal remediation.

However, it is crucial to acknowledge the inherent challenges and limitations of this work. A primary challenge lay in the heterogeneity of the raw materials (coal and biomass), which demanded rigorous quality control measures to ensure experimental reproducibility. The research was also primarily conducted on the laboratory scale using synthetic aqueous solutions for most experiments. While the tests on real laundry wastewater provided a degree of real-world relevance, the performance of these adsorbents in diverse and complex industrial effluents, characterized by varying pH, ionic strength, and competing contaminants, remains to be fully elucidated. Furthermore, the recyclability assessment, while demonstrating initial promise, was limited to five cycles. A more extensive longevity study is necessary to comprehensively gauge the long-term operational viability and potential degradation of the materials.

4.3. Recommendations for Future Research

Building upon the foundations established by this dissertation, several specific and actionable recommendations for future research emerge to bridge the gap between laboratory-scale innovation and practical environmental application:

- **Scale-Up and Pilot Studies:** Transition from batch experiments to continuous flow column studies to rigorously evaluate long-term adsorbent performance, hydraulic characteristics (e.g., breakthrough curves), and operational stability under more realistic flow and loading conditions. Pilot-scale wastewater treatment studies, particularly focusing on complex industrial effluent, are essential for practical validation.
- **Regeneration and Adsorbent Longevity Optimization:** Conduct in-depth investigations into diverse regeneration strategies for both modified coal and NSWR biomass. This should include optimizing elution protocols to recover pollutants, assessing adsorbent structural

integrity across extended regeneration cycles, and rigorously evaluating adsorbent attrition rates to fully determine their long-term operational and economic viability.

- **Techno-Economic Assessment and Life-Cycle Analysis:** Perform detailed cost-benefit analyses comparing these waste-derived adsorbents with existing commercially available water treatment technologies. Such analyses should encompass all aspects of the material lifecycle—from sourcing and production to operation, regeneration, and end-of-life management—to objectively determine their competitiveness and overall environmental footprint.
- **Adsorbent Modification and Target-Specific Design:** Explore alternative modification strategies for both coal and NSWR, investigating different chemical or physical activation methods (e.g., thermal, microwave-assisted) tailored to enhance selectivity and adsorption capacity for specific target pollutants beyond those studied, particularly focusing on other classes of emerging contaminants.
- **Mechanism Elucidation at the Molecular Level:** Employ advanced spectroscopic techniques (e.g., XPS, advanced FTIR) and computational modeling to gain a deeper, molecular-level understanding of adsorbate-adsorbent interactions. This includes precise binding site identification, quantifying the dominant forces, and determining the orientation of adsorbed molecules, which can guide the rational design of next-generation adsorbents.
- **Landfill Remediation Strategy Development:** Conduct targeted and comprehensive field studies to assess the applicability and effectiveness of NSWR biomass for in-situ or ex-situ cadmium remediation in the contaminated Madaba landfill soil. This work should focus on site-specific conditions and optimizing the application method to translate the findings of this dissertation into a tangible, regional environmental benefit.

6. NEW SCIENTIFIC RESULTS

This doctoral research has yielded several novel scientific contributions to the field of environmental remediation and materials science. The primary new findings are summarized as follows:

1. Sulfuric acid modification of sub-bituminous coal was shown to create a novel adsorbent with an exceptionally high maximum adsorption capacity (Q_{max}) of **854.2 mg/g** for the pharmaceutical ciprofloxacin (CFX). This result establishes the modified material as a highly effective adsorbent, providing a new benchmark for valorizing waste coal for pharmaceutical contaminant removal.
2. Unmodified Norway Spruce Wood Residue (NSWR) was established as an effective, low-cost biosorbent for the *simultaneous* sequestration of multiple heavy metals [Pb(II), Cu(II), Cd(II), Zn(II)]. Its efficacy was validated not only in synthetic solutions but also in complex real laundry wastewater, demonstrating its practical potential. Mechanistic studies clarified the distinct removal pathways, with heavy metal uptake governed by chemisorption and ion exchange, while CFX adsorption onto modified coal was dominated by physisorption.
3. Nano-synthesis was proven as a highly effective strategy for performance enhancement. Nanoparticles derived from NSWR biomass (Nano-NSWR) demonstrated a dramatic increase in heavy metal adsorption, with capacities improving up to **89%** for cadmium compared to the original material, quantifying the significant benefit of nano-structuring biosorbents.
4. The research demonstrated that Artificial Intelligence (AI) regression models, particularly XGBoost, can serve as robust and accurate predictive tools for adsorption performance. These models successfully captured complex, non-linear process dynamics, showing their utility as a potent alternative to classical kinetic models in environmental science.
5. A novel link between laboratory materials science and practical environmental management was established. Through a case study of cadmium contamination at the Madaba landfill, the research proposed a direct, sustainable remediation strategy using the developed NSWR biomass as a reactive barrier material in landfill liners, translating laboratory findings into a tangible environmental solution.

PUBLICATIONS RELATED TO THE DISSERTATION

Al-Labadi, I. G., Horváth, M., Alkilani, A. T., Al-Ma'abreh, A. M., Bashir, M., Keshta, B. E., ... & Eid, M. H. (2025). Simultaneous Adsorptive Removal of Pb^{2+}, Cd^{2+}, Cu^{2+}, and Zn^{2+} Using Raw Norway Spruce Biomass: A Low-Cost and Eco-Friendly Solution for Wastewater Treatment. *Frontiers in Water*, *7*, 1612232.

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