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ADSORPTION OF COPPER (II) FROM WASTEWATER USING POLYETHERSULFONE-PINEAPPLE CROWN LEAF COMPOSITE MEMBRANE

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Abstract
Pineapple leaves offer a sustainable alternative to traditional materials, reducing waste and promoting resource efficiency. This readily available resource can empower local communities and create new avenues for economic development. Pineapple crown leaf can be used to develop the potential of a new low cost adsorbent. The adsorbent was made from pineapple crown leaves (a biowaste) combined with polyethersulfone (PES) polymer, titanium dioxide (TiO2) additive, and N,N-dimethylformamide (DMF) solvent. Phase inversion technique was used to prepare the membrane using immersion precipitation. The leaves were pretreated before use. The characterisation analysis using ATR-FTIR displayed characteristics of cellulose from pineapple crown leave and polyethersulfone (PES) polymer. For isotherm study, the membrane was placed in standard solutions with different initial concentrations of the adsorbate (50, 100, 150 and 200 ppm) and stirred each solution to determine the capacity of the new developed adsorbent to adsorb copper heavy metal ions in wastewater at different concentration. Applying the results of the experiment to Langmuir and Freundlich adsorption isotherm equations to grasp the adsorption characteristics of the membrane. As a result, it was found that the adsorption process on pineapple crown leave membrane most likely involves a monolayer, it was best fitted with the Langmuir adsorption isotherm. Additionally, a series of adsorption experiments were conducted at a constant concentration of 1.5 ppm. The adsorption time was varied from 1 minute to 240 minutes to study the adsorption kinetics. The kinetic studies were also performed to clearly demonstrate the adsorption process. The kinetic studies also revealed that the absorption process was governed by the pseudo second-order kinetic model, and pineapple crown leaf membranes show 93% or higher removal rate when adsorption time is 120 mins or higher.
Keywords: adsorption, copper, pineapple crown leave, membrane, polyethersulfone

Introduction

Heavy metal contamination in water resources has become a critical environmental and public health concern due to rapid industrialization, urbanization, and increasing anthropogenic activities. Among various heavy metals, copper is widely used in industries such as electroplating, electronics manufacturing, and plumbing systems, leading to its frequent presence in surface water, groundwater, and drinking water supplies (Fitzgerald, 1998). Although copper is an essential trace element for biological systems, excessive exposure can result in severe toxic effects, including gastrointestinal bleeding, hepatic toxicity, intravascular hemolysis, acute renal failure, and methemoglobinemia (WHO, 2004; Sabarina et al., 2014). The widespread use of copper pipes in domestic plumbing further contributes to copper leaching into drinking water, making its removal from water systems an urgent necessity.

Various treatment technologies have been employed to remove copper ions from wastewater, including chemical precipitation, ion exchange, reverse osmosis, microfiltration, and ultrafiltration (Lee et al., 2022). However, many of these techniques suffer from limitations such as high operational costs, complex system design, membrane fouling, and secondary waste generation. Among the available

treatment methods, adsorption has emerged as one of the most effective and economical approaches due to its simplicity, high removal efficiency, operational flexibility, and minimal production of harmful by-products (Lenka et al., 2021; Marszałek, 2022). Adsorption-based processes have demonstrated strong potential for selective removal of heavy metal ions using a wide range of adsorbents, including biomaterials, activated carbons, polymeric resins, and composite membranes (Gogoi et al., 2018).

In recent years, increasing attention has been directed toward the utilization of agricultural and biowaste materials as sustainable adsorbents to reduce environmental burden while adding value to waste streams. Pineapple crown leaves, an abundant agricultural by-product, are rich in cellulose and possess various functional groups such as hydroxyl, carboxyl, and ether groups that are favorable for metal ion adsorption (Gogoi et al., 2018). Previous studies have demonstrated the effectiveness of pineapple crown leaves for adsorption of heavy metals such as chromium ions, with adsorption behavior strongly influenced by solution pH and surface modification (Gogoi et al., 2018). However, the direct application of raw biomass often faces challenges related to mechanical stability, reusability, and separation from treated water.

To overcome these limitations, the incorporation of biomass-derived adsorbents into polymeric membrane matrices has gained significant interest. Polyethersulfone (PES) is a high-performance thermoplastic polymer widely used in membrane fabrication due to its excellent thermal stability, mechanical strength, and chemical resistance (Fadhilah et al., 2023). PES-based membranes exhibit strong resistance to acids, alkalis, hot water, and organic solvents, making them suitable for wastewater treatment applications. The combination of PES with cellulose-rich biomass materials can enhance membrane adsorption capacity while improving structural integrity and handling properties (Ng et al., 2020). Moreover, cellulose-based membranes are biodegradable and biocompatible, offering an environmentally friendly alternative to conventional synthetic adsorbents (Zhu et al., 2014).

Understanding the adsorption behavior of copper ions on composite membranes requires detailed evaluation of adsorption isotherms and kinetic models. Isotherm studies, particularly Langmuir and Freundlich models, provide insight into the adsorption mechanism, surface homogeneity, and adsorption capacity of the membrane (Lee et al., 2022). Kinetic studies further elucidate the rate-controlling steps of adsorption, distinguishing between physical and chemical adsorption processes through pseudo-first order and pseudo-second-order models (Lenka et al., 2021). Such analyses are essential for assessing the feasibility and efficiency of newly developed adsorbent membranes for practical wastewater treatment applications.

In this study, a novel polyethersulfone–pineapple crown leaf composite membrane was fabricated via the phase inversion technique and evaluated for its ability to remove Cu(II) ions from aqueous solutions. The membrane was characterized using ATR-FTIR to confirm the presence of functional groups responsible for adsorption, while adsorption performance was assessed through isotherm and kinetic studies. By integrating agricultural waste with a robust polymer matrix, this work aims to develop a low-cost, sustainable, and efficient adsorbent membrane for copper removal from wastewater, contributing to resource recovery, waste minimization, and environmental protection.

Materials and methods

Chemicals

Polyethersulfone polymer, NaOH, TiO_2, and $CuSO_4$ was purchased from Merck, Germany. Analytical grade Isopropyl alcohol and dimetheylformamide (DMF) from Sigma Aldrich, USA.

Pretreatment of pineapple crown leaves

The pineapple crown leaves were first thoroughly rinsed with distilled water to remove surface impurities and dirt. The cleaned leaves were then chopped into small pieces and dried in a hot air oven at 70 °C for 24 h. After drying, the leaves were ground using a laboratory grinder to obtain fine particles with an approximate size of 0.1 mm. To remove extractives and enhance cellulose exposure, 30 g of the ground pineapple crown leaves were mixed with 450 mL of 20% (v/v) isopropyl alcohol in an Erlenmeyer flask and stirred continuously for 24 h at room temperature. The mixture was subsequently filtered and washed repeatedly with distilled water until the filtrate became colorless. The residue was then oven-dried at 50 °C overnight. Delignification was carried out by stirring the dried residue with 480 mL of 0.1 mol L^{-1} sodium hydroxide (NaOH) solution for 2 h at room temperature. Following filtration, the treated pineapple crown leaves were washed repeatedly with distilled water until neutral pH was achieved. The pretreated leaves were finally dried overnight at 50 °C and stored in a desiccator for subsequent membrane fabrication.

Fabrication of polyetehrsulfone-pineapple crown leaf composite membrane

The composite membrane was prepared using the phase inversion technique via immersion precipitation, following a procedure adapted from Ng et al. (2020). The casting solution was formulated with a composition of 63.5 wt% DMF, 15 wt% PES, 20 wt% pretreated pineapple crown leaves, and 1.5 wt% TiO_2. Initially, DMF solvent, TiO_2 additive, and pretreated pineapple crown leaves were mixed in a sealed glass bottle and stirred at 60 °C for 30 min to ensure homogeneous dispersion. Subsequently, PES polymer was gradually added to the mixture and stirred continuously at 60 °C for 24 h until a uniform and viscous solution was obtained. The resulting casting solution was left undisturbed for an additional 24 h to allow complete degassing and removal of air bubbles. The casting solution was then spread onto a clean glass plate using a casting blade with a thickness of 50 µm. After brief air exposure for 10 s, the cast film was immediately immersed in a coagulation bath containing distilled water at room temperature for 5 min to induce phase inversion and membrane formation. Upon completion of coagulation, the membrane was rinsed thoroughly with distilled water and stored in water prior to characterisation and adsorption experiments.

Functional group analysis

The functional groups present in the crude pineapple crown leaves, pretreated pineapple crown leaves, and the fabricated composite membrane were analysed using Attenuated Total Reflectance–Fourier Transform Infrared (ATR-FTIR) spectroscopy. Spectra were recorded over a wavenumber range of 4000–400 cm^{-1} to identify characteristic absorption bands associated with cellulose, PES, and other functional groups relevant to metal ion adsorption.

Adsorption isotherm studies

Adsorption isotherm experiments were conducted to evaluate the copper adsorption capacity of the composite membrane at equilibrium. Membrane samples were immersed in copper standard solutions with initial Cu(II) concentrations of 50, 100, 150, and 200 ppm. The solutions were stirred at a constant speed of 230 rpm and maintained at 35 °C for 4 h to ensure equilibrium conditions. After the adsorption process, the membranes were removed, and the residual copper concentration in the solutions was measured using Flame Atomic Absorption Spectroscopy (FAAS). The adsorption capacity and removal efficiency were calculated accordingly. The equilibrium adsorption data were analysed using Langmuir and Freundlich isotherm models. The Langmuir model assumes monolayer adsorption on a homogeneous surface with finite adsorption sites, while the Freundlich model describes adsorption on heterogeneous surfaces with non-uniform energy distribution (Lee et al., 2022). The suitability of the adsorption process was further evaluated using the dimensionless separation factor (R^L).

Adsorption kinetic studies

Adsorption kinetic experiments were performed to investigate the effect of contact time on copper removal efficiency. The experiments were carried out at a fixed initial Cu(II) concentration of 1.5 ppm, while the contact time was varied from 1 min to 240 min. All experiments were conducted under constant stirring conditions, and samples were collected at predetermined time intervals. The amount of copper adsorbed at time t (q_t) and at equilibrium (q_e) was calculated based on the measured copper concentrations using FAAS. The kinetic data were analysed using pseudo-first order and pseudo-second order kinetic models to determine the rate-controlling mechanism of the adsorption process (Lee et al., 2022). The goodness of fit of each model was assessed using the correlation coefficient (R^2).

Results and discussion

Functional group characterization

The functional groups present in crude pineapple crown leaves, pretreated pineapple crown leaves, and the fabricated polyethersulfone–pineapple crown leaf composite membrane were analysed using ATR-FTIR spectroscopy to elucidate structural changes resulting from pretreatment and membrane fabrication as shown in Figure 1.. The FTIR spectra of crude and pretreated pineapple crown leaves exhibited broad absorption bands in the range of 3317–3330 cm^{-1}, corresponding to the stretching vibration of hydroxyl (–OH) groups associated with cellulose. These hydroxyl groups play a crucial role in metal ion adsorption through hydrogen bonding and coordination interactions. Peaks observed at approximately 2920 cm^{-1} were attributed to C–H stretching vibrations, while absorption bands around 1730–1740 cm^{-1} indicated the presence of C=O stretching vibrations associated with carboxylic functional groups. Additional peaks near 1031 cm^{-1} were assigned to C–O–C vibrations and glycosidic linkages between glucose units in cellulose, confirming the cellulose-rich nature of the pineapple crown

leaves, consistent with previous reports (Bolio-López et al., 2016).

Following alkaline pretreatment, minor shifts and intensity changes in the FTIR spectra were observed, indicating partial removal of lignin and enhanced exposure of cellulose functional groups. The reduction of lignin-related components increases the availability of active adsorption sites, thereby improving metal ion binding potential. The FTIR spectrum of the fabricated composite membrane revealed characteristic absorption peaks corresponding to both cellulose and polyethersulfone (PES), confirming successful incorporation of pineapple crown leaf biomass into the polymer matrix. Distinct peaks at 1232 cm^{-1} and 1101 cm^{-1} were attributed to C–O–C and O=S=O stretching vibrations of PES, respectively, while aromatic C=C stretching vibrations appeared around 1575 cm^{-1} and 1448 cm^{-1}. The presence of aromatic C–H vibrations near 833 cm^{-1} further confirmed the PES structure. Additionally, a peak at approximately 1146 cm^{-1} was associated with residual DMF solvent used during membrane fabrication. The coexistence of cellulose- and PES-related functional groups indicates the formation of a composite membrane with multiple active sites suitable for Cu(II) adsorption.

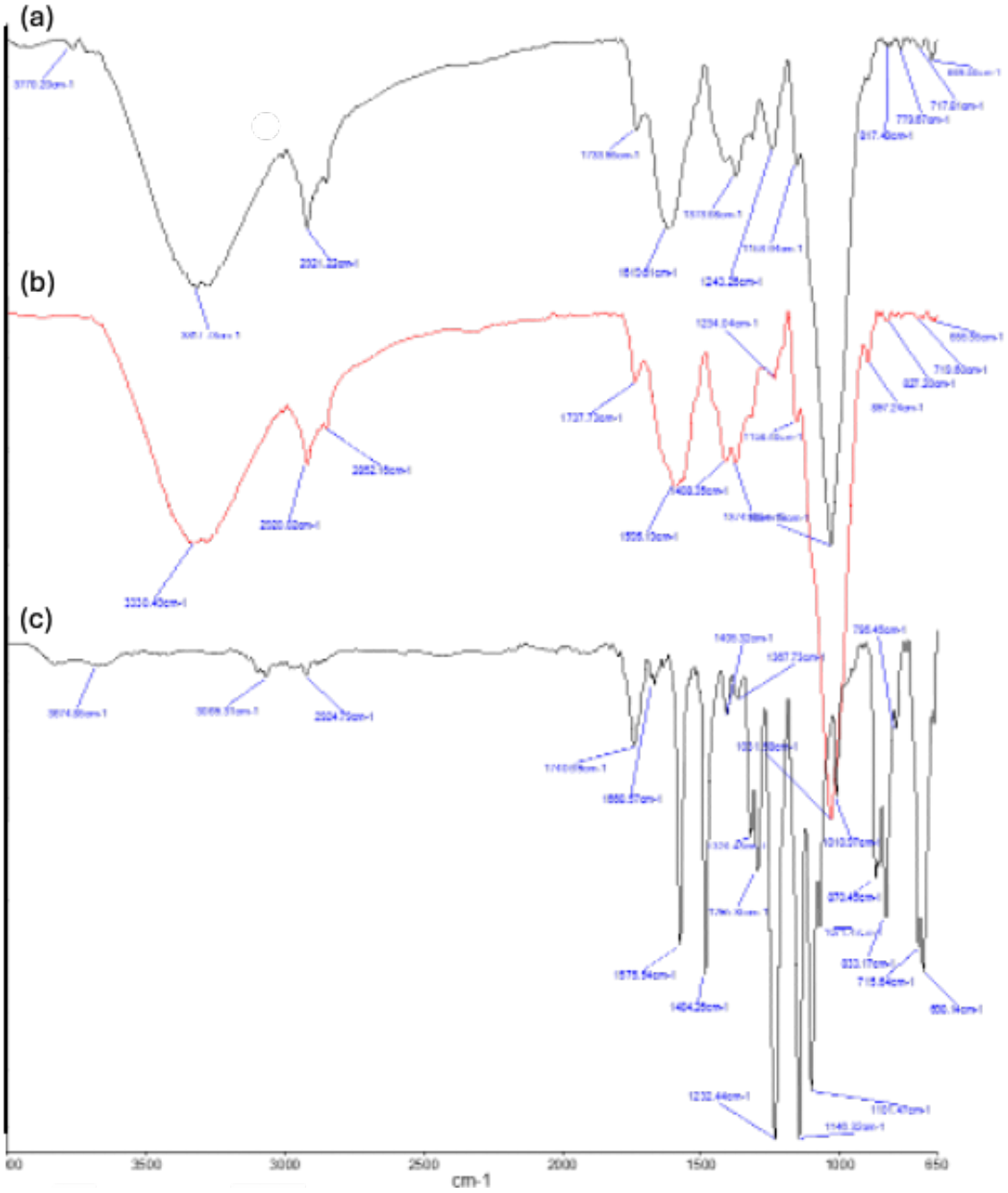

Figure 1 FTIR spectra for (a) raw pineapple leaves, (b) pretreated pineapple leaves, and (c) neat PES membrane.

Adsorption isotherm behaviour of Cu^{2+} ions

The adsorption performance of the composite membrane was evaluated by conducting equilibrium adsorption experiments using Cu(II) solutions with initial concentrations of 50, 100, 150, and 200 ppm. The membrane exhibited high copper removal efficiencies at lower concentrations, achieving removal rates of 86.43% and 83.24% at 50 ppm and 100 ppm, respectively. However, a noticeable decrease in removal efficiency was observed at higher concentrations of 150 ppm and 200 ppm. This trend can be attributed to saturation of available adsorption sites on the membrane surface. At lower copper concentrations, abundant active sites are available, allowing efficient binding of Cu^{2+} ions. As the concentration increases, these sites become progressively occupied, limiting further adsorption and reducing overall removal efficiency.

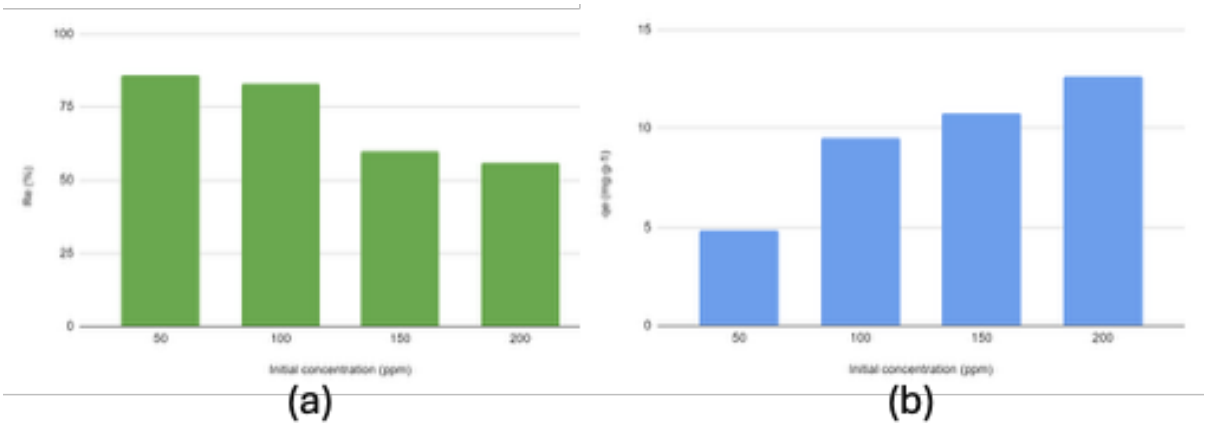

Figure 2 (**a**) Removal efficiency and (b) adsorption capacity of pineapple crown leave membrane.

To further elucidate the adsorption mechanism, the equilibrium data were analysed using Langmuir and Freundlich isotherm models. According to Figure 3 and Figure 4, the Langmuir isotherm model demonstrated a higher correlation coefficient (R^2= 0.946) compared to the Freundlich model (R^2 = 0.927), indicating that the adsorption process is better described by the Langmuir model. This suggests that Cu(II) adsorption occurs predominantly as a monolayer on a homogeneous membrane surface with finite and energetically equivalent adsorption sites. The calculated maximum adsorption capacity (q_{max}) of 24.735 mg g^{-1} reflects the strong affinity of the composite membrane toward copper ions. Furthermore, the dimensionless separation factor (R^L) value of 0.0063 falls within the range of 0 < R^L < 1, confirming that the adsorption process is favorable under the studied conditions as summarized in Table 1. These findings are consistent with adsorption behavior reported for other biomass-based composite membranes used for heavy metal removal (Lee et al., 2022; Lenka et al., 2021).

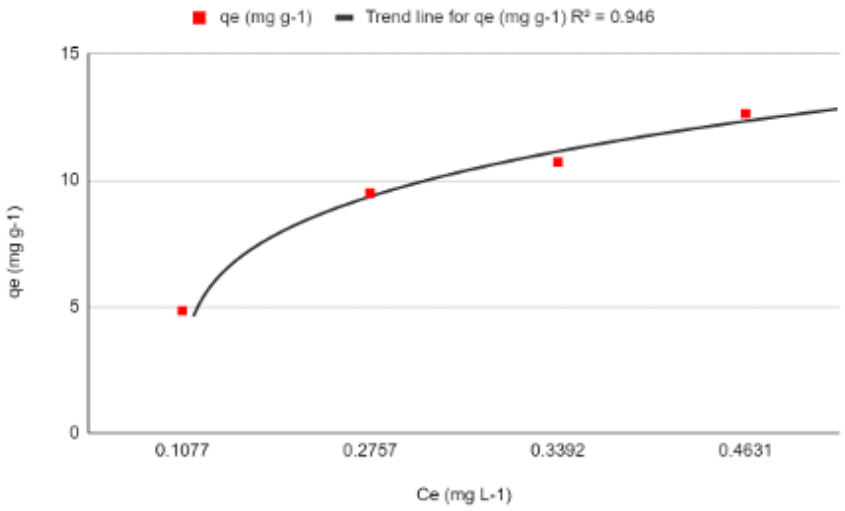

Figure 3 Langmuir isotherm for Cu(II) adsorption..

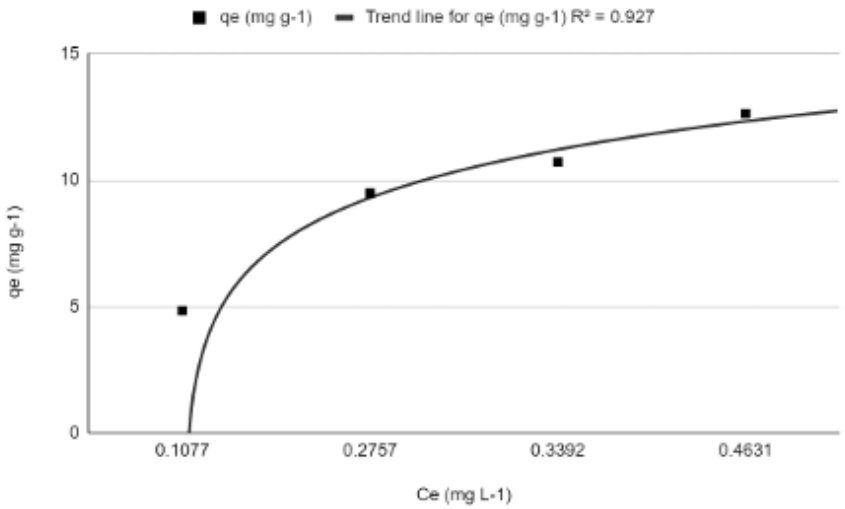

Figure 4 Freundlich isotherm for Cu(II) adsorption.

Table 1: Adsorption isotherm parameters obtained from Langmuir and Freundlich models for Cu(II) removal.

Isotherm model	Parameter	Value
Langmuir	q_{max}	24.735
	K_L	2.256
	R_L	0.0063
	R^2	0.946
Freundlich	K_F	12.42
	1/n	0.1873
	R^2	0.927

Adsorption kinetics and removal efficiency

The effect of contact time on Cu(II) removal (Figure 5) was investigated at a fixed initial concentration of 1.5 ppm over a time range of 1 to 240 min. The results demonstrated a rapid increase in copper removal efficiency during the initial stage of adsorption, followed by a gradual approach toward equilibrium. The membrane achieved a removal efficiency exceeding 93% after 120 min, indicating highly effective copper uptake within a relatively short contact time. The rapid initial adsorption can be attributed to the availability of a large number of vacant adsorption sites and strong electrostatic attraction between Cu(II) ions and functional groups on the membrane surface. As adsorption progresses, the rate decreases due to site saturation and reduced driving force for mass transfer.

The kinetic data were analysed using pseudo-first order and pseudo-second-order kinetic models to identify the rate-controlling mechanism as shown in Figure 6. The pseudo-second-order model provided an excellent fit to the experimental data, with a high correlation coefficient (R^2 = 0.998), significantly exceeding that of the pseudo-first-order model (R^2 = 0.964). Additionally, the equilibrium adsorption capacity calculated from the pseudo-second-order model closely matched the experimentally obtained value. This strong agreement suggests that chemisorption is the dominant mechanism governing Cu(II) adsorption onto the composite membrane. Chemisorption involves valence forces through sharing or exchange of electrons between copper ions and functional groups such as hydroxyl and carboxyl groups present in the cellulose matrix, reinforcing the strong binding observed during adsorption (Lenka et al., 2021).

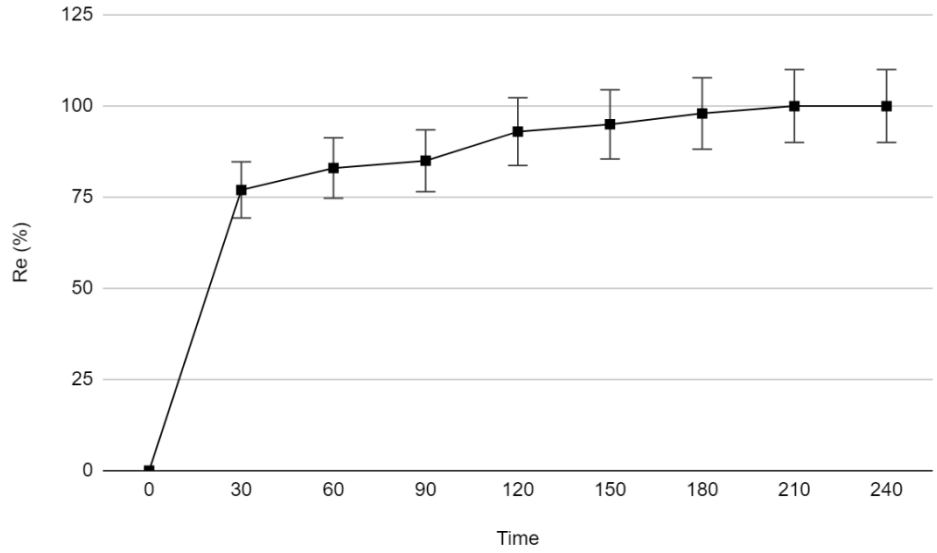

Figure 5 Effect of contact time on the removal of Cu(II) by adsorption onto adsorbents.

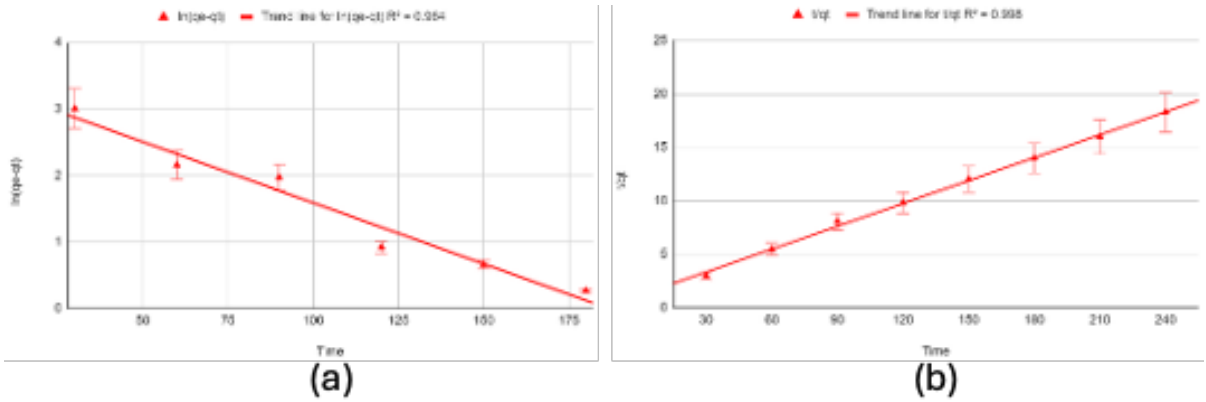

Figure 6 (a) Pseudo-first order and (b) pseudo-second-order kinetic curves for Cu(II) adsorption on adsorbents

Table 2: Kinetic model parameters for Cu(II) adsorption.

Kinetic model	Parameter	Value
Pseudo-first order	$q_{e,exp}$	13.135
	k_1	0.0492
	$q_{e,cal}$	4.479
	R^2	0.964
Pseudo-second order	$q_{e,exp}$	13.135
	k_2	0.0547
	$q_{e,cal}$	13.142
	R^2	0.998

Overall adsorption performance and mechanistic implications

The combined isotherm and kinetic analyses indicate that the polyethersulfone–pineapple crown leaf composite membrane exhibits strong adsorption performance for Cu(II) removal, particularly at low concentrations relevant to wastewater treatment applications. The predominance of Langmuir-type adsorption suggests uniform adsorption sites and monolayer coverage, while pseudo-second-order kinetics confirm that chemical interactions govern the adsorption process. The integration of cellulose-rich pineapple crown leaves within a robust PES matrix provides both high adsorption efficiency and

structural stability, overcoming common limitations associated with raw biomass adsorbents. These results demonstrate the potential of agricultural biowaste-derived composite membranes as sustainable and effective materials for heavy metal removal from wastewater, aligning with global efforts toward waste valorisation and environmentally friendly water treatment technologies.

Conclusion

S A sustainable polyethersulfone–pineapple crown leaf composite membrane was successfully fabricated via the phase inversion technique and evaluated for Cu(II) removal from aqueous solutions. ATR-FTIR analysis confirmed the incorporation of cellulose-based functional groups from pineapple crown leaves into the polyethersulfone matrix, providing active sites for metal ion adsorption. The composite membrane exhibited high copper removal efficiency, exceeding 83% at initial concentrations of 50–100 ppm and achieving over 93% removal at low Cu(II) concentration after 120 min of contact time. Equilibrium adsorption data were best described by the Langmuir isotherm model, indicating monolayer adsorption with a maximum adsorption capacity of 24.735 mg g^{-1}, while kinetic analysis revealed that the adsorption process followed a pseudo-second-order model, suggesting chemisorption as the dominant rate-controlling mechanism. These findings demonstrate the potential of pineapple crown leaf-based composite membranes as low-cost, efficient, and environmentally friendly adsorbents for copper removal in wastewater treatment applications.

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