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Sustainable Removal of Cu^{2+} and Pb^{2+} Ions via Adsorption Using Polyvinyl Alcohol/Neem Leaf Extract/Chitosan (From Shrimp Shells) Composite Films

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ABSTRACT: The purpose of this research work is to determine the removal efficiency of Cu^{2+} and Pb^{2+} ions using polyvinyl alcohol/neem leaf extract/chitosan (PVA/NLE/CS) composite films as adsorbent materials from an aqueous medium, with respect to pH, contact time, and adsorbent dosage. The synthesized composite material was characterized using Fourier Transform Infrared (FTIR) spectroscopy, thermogravimetric analysis-Derivative Thermogravimetry (TGA-DTG), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDX). The antibacterial activity and swelling response of the material were studied using suitable methodologies. The FTIR study confirmed the interactions among PVA, chitosan, and neem leaf extract. The TGA data reveal the excellent thermal stability of the developed composite films. The SEM micrograph indicates a homogeneous phase morphology with good compatibility among chitosan, the monomer, and the leaf extract. The antibacterial study revealed that the prepared PVA/NLE/CS films exhibit improved antibacterial activity against bacterial growth. It was found that at pH 6.0, the adsorption capacity for both toxic metal ions is maximum, and decreases with a further rise in pH. At this pH, the adsorption capacity of PVA/NLE/CS films increases with a gradual increase in adsorbent dosage, and at a specific pH, the adsorption capacity for Cu^{2+} is greater than that for Pb^{2+} . The adsorption efficiency is a function of contact time and was found to be maximal at 180 min. Hence, the developed composite material is effective for the removal of metal ions from wastewater.

KEYWORDS: Neem leaf extract; chitosan; polyvinyl alcohol (PVA); antibacterial activity; adsorption capacity

Highlights:

- Neem leaf-based hybrid composite film is developed using a polyvinyl alcohol (PVA) matrix, reinforcing both chitosan and neem leaf powder.
- The synthesized hybrid composite material is highly effective for the removal of Cu^{2+} and Pb^{2+} ions from water through adsorption.
- The tendency of removal of metal ions increases with an increase in adsorbent dosage and follows the order $\text{Cu}^{2+} > \text{Pb}^{2+}$.
- The adsorption process can be better explained by the Langmuir adsorption isotherm, than the Freundlich adsorption isotherm and follows pseudo-second-order kinetics.



1 Introduction

The industrial and mining wastewater mostly contains a noticeable concentration of potentially toxic metal ions of various kinds, with toxic organic pollutants that not only cause a health hazard impact on human beings but also severely affect the environment [1].

The remediation of toxic metal ions from the polluted water and industrial effluents is a challenge to researchers [2,3]. Copper and lead are two significant heavy metals commonly found in industrial wastewater, and both cause serious health risks to humans. Natural sources include soil erosion and the weathering of copper-bearing rocks, while industrial contributions come from electronics manufacturing, mining operations, metal plating, and the corrosion of brass and copper plumbing materials [4]. While copper is an essential mineral for human health, excessive exposure beyond acceptable limits can lead to various serious health issues, including gastrointestinal, neurological, and cardiovascular disorders, as well as liver damage, nausea, vomiting, and diarrhoea [5,6]. Lead contamination in wastewater primarily results from the corrosion of lead-based plumbing systems, as well as activities such as electroplating, battery production, and metal smelting. The use of lead-contaminated drinking water severely affects multiple body systems, specifically the brain, liver, nervous system, kidney, bones, and teeth. It is specifically toxic to pregnant ladies and young children [7,8]. Various human activities contribute to the release of heavy metals into the environment. These include mining, the use of fertilizers, pesticides, and herbicides in agriculture, as well as the discharge of inadequately treated or untreated industrial effluents and sewage water [9–11]. For instance, mercury enters aquatic systems through industrial processes such as coal combustion, chlor-alkali production, gold mining, pharmaceutical manufacturing, and the improper disposal of mercury-containing items like electronic waste and fluorescent bulbs [12,13]. Similarly, cadmium pollution in the environment is largely driven by its use in battery manufacturing, pigments, metal plating, and textile production [14]. Polymer hydrogels are widely employed as efficient adsorbents for heavy metals due to the presence of amino and hydroxyl groups, which enable strong binding interactions with metal ions [15]. Zeolites are also utilized to adsorb heavy metals such as mercury (Hg), cadmium (Cd), and lead (Pb). Activated carbon serves as an effective adsorbent for removing metals like copper (Cu), chromium (Cr), lead (Pb), zinc (Zn), and cadmium (Cd) [16]. Other frequently used adsorbents include carbon-based substances such as graphene and carbon nanotubes, as well as clay materials like montmorillonite (MMT), bentonite, and kaolinite [17,18]. Common bioadsorbents include chitosan, red mud, agricultural residues (e.g., rice husk, sugarcane bagasse, wheat straw), plant biomass, and algal biomass [19]. The application of low-cost, eco-friendly sorbents for eliminating hazardous metals from contaminated water is now a promising global issue. Because of the demand of seafood throughout the world, the volume of shrimp shell waste gradually increases, which on degradation, results negative impact to human beings and the surrounding environment. The dried shrimp shell wastes contain about 40%–50% of chitin, which on deacetylation is converted into chitosan [20]. Chitosan and its composite materials are widely used in various sectors, specifically biomedical, tissue engineering, packaging, cosmetics, wound healing, drug delivery, textile miniaturizing, and water treatment. The chitosan-based biomaterials possess the capability of remediating potentially toxic metals from wastewater through adsorption. The superior adsorption capability of chitosan-based materials is due to the presence of some active nitrogen sites in the chitosan molecule [21]. The mechanism and efficiency of adsorption of the biocomposite material depend on physical, bacteriological, and chemical parameters of the groundwater of the study area that include redox potential, pH, cations, anions of inorganic and organic materials, and kinds of other metal ions present. Polyvinyl alcohol (PVA) is a known synthetic polymer which is non-toxic, water-soluble, biodegradable, and biocompatible. PVA has drawn a lot of attention because of some of its unique properties, including cost-effective, non-toxic, biocompatible, highly durable, chemically stable, controlled drug delivery, and membrane preparations [22]. The large number

of hydroxyl groups (-OH) present in PVA serves as the active site for blending the additive materials and facilitates the formation of the composite [23–25]. Kumar et al. in 2019 synthesized a nanocomposites film of chitosan/PVA/ZnO, which is used for the removal of organic dyes [26]. Wang et al. in 2025 developed a hydrogel based on PVA, chitosan and studied its application as flexible sensors [27]. Dewanjee et al. in 2025 developed a PVA/Chitosan based hydrogel reinforcing ZnO and cellulose and studied its biomedical applications [28]. Although numerous studies have been carried out based on PVA/chitosan composites, but the novelty of this research work is that the composite material [PVA/neem leaf extract/chitosan (PVA/NLE/CS)] developed is completely new, and two naturally obtainable materials (chitosan derived from shrimp shell and neem leaf extract) are used as reinforcing materials. The use of shrimp shell waste not only forms a new biomaterial but also reduces the pollution load of the environment [29]. The composite material reinforced with NLE demonstrates excellent antimicrobial properties, enhanced thermal stability, sufficient mechanical strength, and biodegradability [30]. The presence of bioactive compounds in NLE, such as nimbin and azadirachtin, contributes to its improved antimicrobial performance. As a result, the composite effectively inhibits the growth of fungi, bacteria, and other microorganisms, making it more resistant to contamination and spoilage. This makes the biocomposite particularly suitable for packaging applications, especially in food packaging, as it helps extend the shelf life of the packaged products.

Furthermore, an innovative new film was designed using these composite materials, and its efficiency in separating Pb^{2+} and Cu^{2+} ions from wastewater was studied by adopting suitable methodology. This study evaluated the impact of specific factors, including adsorbent dosage, pH, and contact time. Additionally, various isotherm models were utilized to compare the experimental results with the theoretical data derived from these models.

2 Materials and Methods

2.1 Materials

Polyvinyl alcohol (PVA) was purchased from Central Drug House Pvt. Ltd. Double-distilled water was prepared in the laboratory. Shrimp shells are collected from the local market, Burla. Neem leaves are collected from the neem trees of the local area. Copper nitrate and lead nitrate were purchased from Lab India, Bhubaneswar.

2.2 Preparation of Neem Leaf Extracts (NLE)

The collected neem leaves (*Azadirachta indica*) were properly cleaned with distilled water and then with ethanol to remove dust particles and other contaminants. The leaves were oven-dried at 45°C for 5–6 h till they became brittle. After that, the dried neem leaves were crushed into fine powdered form with the help of a mechanical grinder. The neem powder was then kept in a muffle furnace for about 3–4 h at 250°C for complete drying. The neem leaves changed into a dark green colour and were utilized as filler in the development of the composite film [31].

2.3 Extraction of Chitosan from Shrimp Shells

The shrimp shells were collected and properly cleaned with pure water three times to eliminate the undesired salts, impurities, and surface stains. Then the shells were broken into small pieces by hand and then completely made dry at 60°C for about 48 h; after that, the dry mass of shrimp shells was sieved with a 30-mesh sieve. Chitosan was extracted from the shrimp shell by carrying out various steps such as demineralization, deproteinization, and deacetylation. The process of demineralization was carried out by the addition of 10 g of dried shrimp shell powder to 100 mL of dilute HCl (2 M) with continuous stirring for

three hours at 25°C. The residue formed was washed using distilled water and then properly filtered using Whatman 42 filter paper. Then the residue obtained was added to 100 mL of 2.5 M NaOH for 5 h at 50°C. The protein present in the residue was removed through filtration and cleaned by washing three times with distilled water. After that, the residue was dehydrated twice with ethanol (95%) and dried overnight at 50°C using an air oven to get chitin. Then chitin obtained was subjected to alkaline deacetylation using a 40% (w/v) NaOH solution. Then the chitosan, which is a deacetylated form of chitin, was thoroughly filtered, clearly washed with distilled water, and then made dry to get pure chitosan. Fig. 1 represents the extraction of chitosan from shrimp shells [32]. The synthesis of chitosan from chitin is represented in Scheme 1.

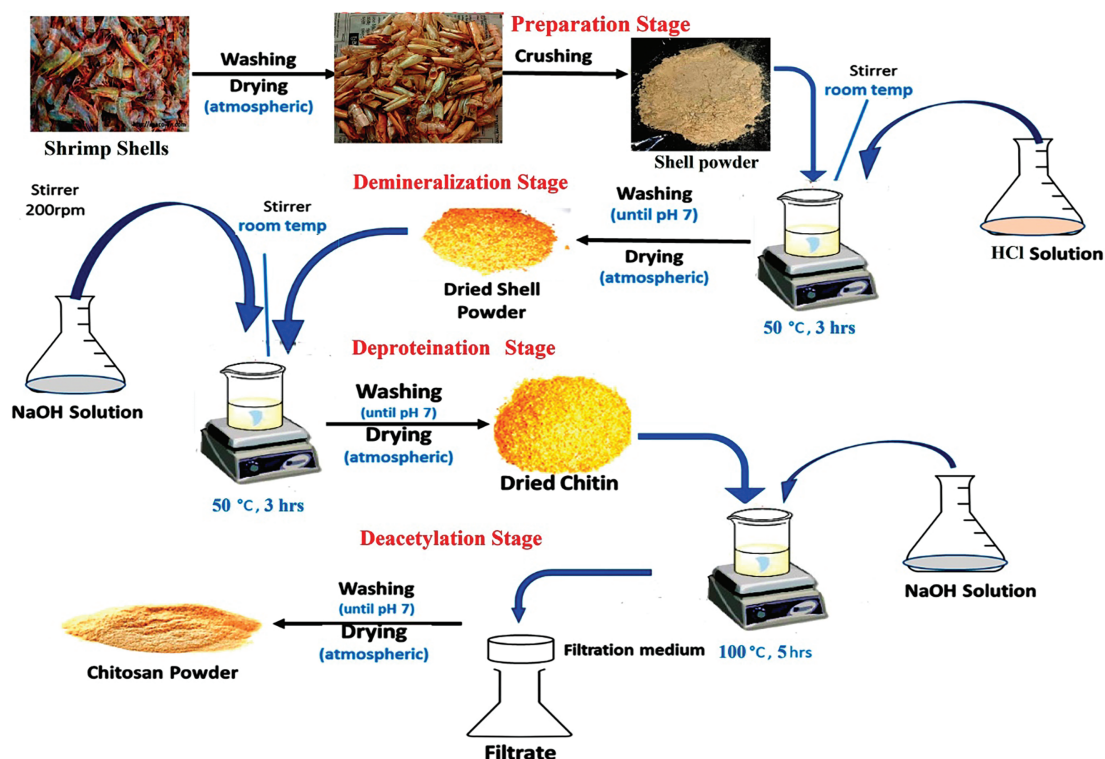
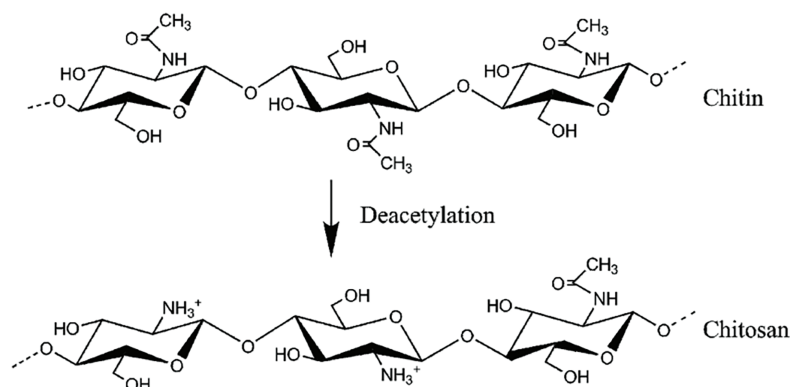


Figure 1: Schematic diagram for Chitosan extraction from shrimp shells



Scheme 1: Deacetylation of chitin to form chitosan

2.4 Preparation of PVA/NLE/CS Composite Films

The solvent casting method was utilized to fabricate the composite film by incorporating NLE into the PVA/CS matrix for reinforcement. In this process, chitosan (0.5 g) was combined with 25 mL of a 2% (v/v) solution of CH_3COOH and stirred continuously for about 1 h. Then 1.6 g of PVA and double-distilled (16 mL) water were added to the solution with continuous stirring for about 45 min. After that, both PVA and CS solutions were taken in the reaction vessel with continuous stirring for about 6 h at 60°C until a clear solution. Then 0.1 g of NLE was added to the PVA/CS solution mixture and continuously stirred for approximately eight hours. The solution was placed in a clean, uncontaminated Petri dish and dried at 45°C in a sealed oven to remove the excess solvent. Fig. 2 represents the synthesis pathway of the PVA/NLE/CS composite films [33].

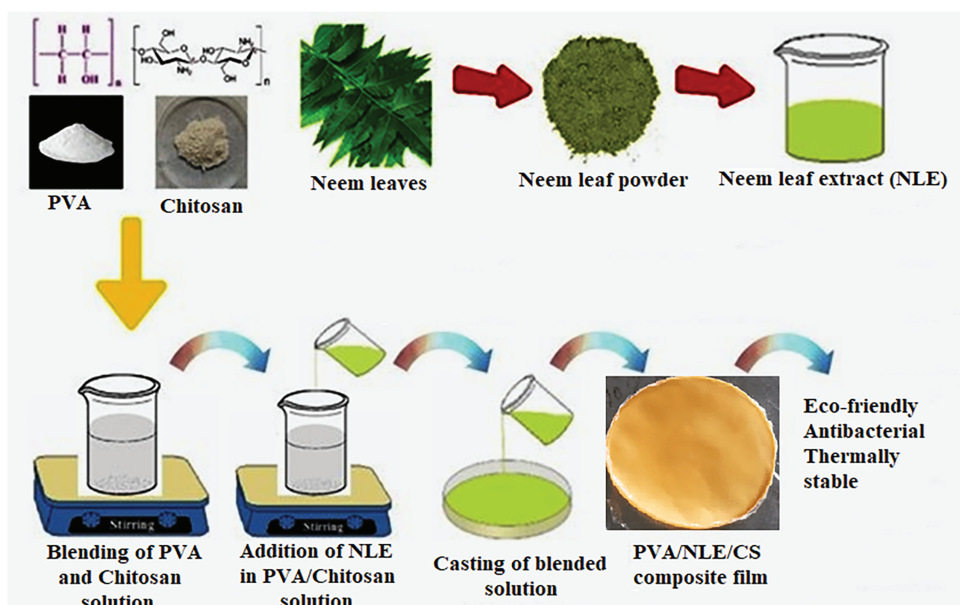


Figure 2: Synthesis process of PVA/NLE/CS composite films

The higher the casting volume of the film-forming solution, the greater the thickness of the composite material after evaporation of the solvent. The higher casting volume increases the probability of homogeneous distribution of various components within the composite material [34]. The rate of drying of the composite material increases with an increase in exposed surface area because of an increase in the rate of evaporation of the solvent. The increase in surface area influences the morphology and increases the microstructure of the composite material. The drying condition depends on various factors such as temperature, humidity, duration of drying, and overall structure of the composite material [35]. The casting volume and thickness of PVA/NLE/CS composite with varying composition ratios are provided in Table 1.

Table 1: Feed composition of PVA/NLE/CS

Hydrogel code	PVA wt.%	NLE wt.%	CS wt.%	Thickness (mm)
PVA70/NLE10/CS20	70	10	20	0.236 ± 0.003
PVA60/NLE10/CS30	60	10	30	0.208 ± 0.004
PVA50/NLE10/CS40	50	10	40	0.188 ± 0.002

2.5 Fourier Transform Infrared Analysis (FTIR)

The FTIR study of PVA/NLE/CS composite films was conducted using an FTIR spectrophotometer (Nicolet iS50) with a resolution range of 4000–400 cm^{-1} with 16 scans at 27°C temperature.

2.6 Thermogravimetric Analysis (TGA)

The TGA analysis of the composite films was done using the instrument from Perkin Elmer, USA. An alumina crucible containing 6–10 mg of the sample was heated to 30°C–600°C, maintaining a flow rate of approximately 10 $\text{min}/^{\circ}\text{C}$ in an inert nitrogen atmosphere.

2.7 Scanning Electron Microscopy (SEM)

The morphological study of the extracted chitosan and composite films (before & after adsorption) was examined using SEM (SEM, Model: JSM-7600F, Jeol Ltd., Tokyo, Japan) at a magnification of X500 and an operating voltage of 5 kV.

2.8 X-Ray Diffraction (XRD)

The XRD diffractograms for extracted CS, NLE, PVA, and composite film material were studied using XRD (Rigaku D/Max-IIA, Tokyo, Japan). The radiation was produced from a Cu $K\alpha$ source operating at 30 kV and 20 mA, with measurements taken in the 2θ range of 10° – 60° , scanning at a speed of $2^{\circ}/\text{min}$.

2.9 X-Ray Photoelectron Spectroscopy (XPS)

The mechanism of adsorption of the PVA/NLE/CS composite films was analysed before and after the adsorption of Cu^{2+} and Pb^{2+} ions, and was measured through XPS (PHI-5000, Ulvac-Phi, Japan).

2.10 Swelling (%)

The dried mass of the material was converted into the required small pieces (15–20 mg) manually. The swelling properties of the synthesized PVA/NLE/CS composite films were evaluated by immersing the sample in distilled water. Each piece of the sample was immersed in 50 mL of distilled water, maintaining a constant temperature of 30°C. After the specified time, the sample pieces of the material were taken from the container, wiped using tissue paper, and then the sample was weighed using an electronic weighing balance. This process was repeated from 10 to 160 min till the equilibrium swelling point was achieved. Eq. (1) is used to calculate the degree of swelling [36].

$$\text{Swelling (\%)} = \frac{W_t - W_o}{W_o} \times 100 \quad (1)$$

where, W_o = Weight of dried sample (before absorption),

W_t = Weight of the swelled sample (after absorption).

2.11 Antibacterial Study

In the antibacterial study, the agar plate method was used to know about the *in vitro* antibacterial efficacy of PVA/NLE/CS films. The antibacterial properties of the films were tested against two distinct bacterial strains, such as *Escherichia coli* (g-positive) and *Staphylococcus aureus* (g-negative bacteria). The samples of material were seeded by Petri plates with agar medium, and the dishes were incubated for about five hours at 30°C. The film, having a 0.02 mg/mL concentration of composite material, was made by dissolving it in a solvent (DMSO). The solutions were then injected into 1 mm sterile discs, which were subsequently placed

onto bacterial plates that had been inoculated. Streptomycin, a known antibacterial agent, was found for comparison. The plates designed were incubated at the optimum temperature of 37°C for bacterial growth and survival. Antibacterial activity was assessed by observing the inhibition zones nearby the wells, and the diameter of these zones was measured using a pachymeter. The mean and standard error of the calculated experimental data were noted, and all incubations were carried out in duplicate [37].

2.12 Adsorption Experiment

The batch adsorption experiments were performed by adjusting and optimizing physical parameters, including the contact time, dose response of adsorbent, and pH. In this study, the replicates used in each adsorption experiment are three. The hypothesis testing (*t*-test) is used to compare between the concentration of the metals before and after adsorption. The capability of adsorption depends on variation in conditions such as adsorption dosage, pH, and time interval. These experimental analyses were carried out under varying conditions, including contact times ranging from 5 to 250 min, pH between 2 and 8, and PVA/NLE/CS with dosages of 0.1–0.6 g/100 mL. A standard solution with a 0.02 g/100 mL concentration was used to maintain the adsorbent dose. Then 0.05 g of the developed PVA/NLE/CS films was submerged in a conical flask containing 100 mL of solution with the addition of 70 mg/L of metal nitrate salt, carefully in the same vessel to quantify the Cu²⁺ and Pb²⁺ concentration in the water samples. To attain the adsorption saturation of the metal ion (Cu²⁺ and Pb²⁺) of the prepared sample of water, the solution was thoroughly shaken for about 4 h at 25°C, and then kept still for 24 h. The metal ion concentrations were determined by AAS (ICE 3000 Series AA Spectrometer–Thermo Scientific) at a wavelength of 279 nm. Each experiment was conducted in two trials, and the mean value of the two trials was considered the optimum value. The efficiency of metal ion adsorption was estimated using Eq. (2), and the % of metal ion removal was calculated using Eq. (3).

$$q = \frac{(C_i - C_f) \times V}{W} \quad (2)$$

$$\text{Removal (\%)} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (3)$$

where, *q* = Adsorption capacity (mg/g) at equilibrium (mg/g)

C_i = Initial concentration of metal ions (mg/L)

C_f = Final concentration of metal ions present in the water sample

V = Volume of the solution prepared water sample in mL

W = Dry weight of the synthesized film.

The buffer solution of different pH was formulated by the following methodology.

A solution with pH 2 was prepared by mixing 0.1 M HCl to a 0.1 M KCl solution. Buffer solutions having pH 3, 4, 5, and 6 were formed by combining 0.1 M citric acid with 0.1 M C₆H₉Na₃O₉. For pH 7 and 8, the required buffer solutions were made by adding 0.1 M HCl, 0.1 M Na₂HPO₄, and 0.1 M NaOH. The prepared buffer solutions were adjusted to 0.1 M, where citric acid serves as a suitable active site for metal ion absorption of the water sample without altering the properties of the water sample [38].

2.13 Competitive Adsorption of Metal Ions on PVA/NLE/CS Composite

The competitive adsorption behaviour of Cu²⁺ and Pb²⁺ ions were examined in an aqueous solution where both ions were present at an equal concentration of 70 mg/L. Under identical conditions, the adsorption

capacity for each metal ion decreased compared to their individual adsorption scenarios. By comparing the separate adsorption capacities Cu^{2+} (61.5 mg/g) and Pb^{2+} (52.08 mg/g), the competitive adsorption capacities increased to 37.1 mg/g for Cu^{2+} and 31.35 mg/g for Pb^{2+} , reflecting a decrease of approximately 65%. This indicates that the presence of one metal ion significantly affects the adsorption behaviour of the other. Overall, the competitive adsorption affinity follows the order: $\text{Cu}^{2+} > \text{Pb}^{2+}$. As shown in Fig. 3, the adsorption capacities of both metal ions under competitive and non-competitive conditions were depicted.

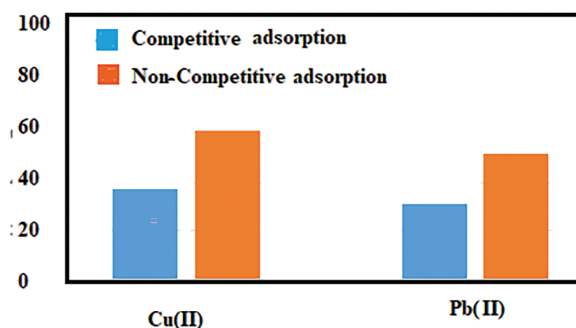


Figure 3: The adsorption capacities of Cu^{2+} and Pb^{2+} under competitive and non-competitive conditions

2.14 Effect of Coexisting Water Ions on Adsorption

The presence of excess ions in water leads to competition with the target ions (Cu^{2+} and Pb^{2+}) for the same adsorption sites on the adsorbent surface. These coexisting ions notably affect the adsorption process by enhancing the adsorption capacity of the target ions. This effect is attributed to factors such as the availability of adsorption sites, a change in surface charge, and alterations in the solvation characteristics of both the adsorbent and the adsorbate.

2.15 Adsorption Isotherm

The experiments based on adsorption isotherm were done under similar conditions as the above-mentioned methodology, utilizing the Freundlich and Langmuir isotherm with a constant pH of 6 and maintaining a contact time of 3 h.

3 Results and Discussion

3.1 Cross-Linked Network of Hydrogel

Numerous techniques of crosslinking have been adopted for the formulation of composite materials through physical and chemical methods. In the chemical method, the polymer chain molecules are cross-linked by the creation of a covalent linkage between them, whereas in the physical method, the polymer chains are cross-linked by the physical interaction between the polymer molecules. The solubility of the material is inhibited because of crosslinking in between the polymer chain molecules. Recently, the formation of hydrogel through physical crosslinking has been focused on, where the cross-linking drastically enhances the interaction between the polymer molecules, which facilitated the formation of hydrogel [39]. The hydrogel formed by physical crosslinking mainly depends on two conditions as follows:

- The intermolecular interaction between the polymer chains is so strong that it can create semi-permanent junctions.
- The structural features of the polymer chain must permit sufficient water to penetrate into the polymeric materials.

3.2 FTIR Analysis

Fig. 4 illustrates the FTIR spectrum of the extracted chitosan, pure PVA, NLE, and the composite film. In the FTIR spectrum of chitosan, a distinct broad absorption peak appears at 3396 cm^{-1} , corresponding to the stretching vibrations of -NH_2 and -OH groups in the parent chain. Additionally, the spectrum reveals a broad and intense absorption peak at 3396 cm^{-1} , because of the stretching vibrations of these functional groups [40]. The presence of amide groups I and III is confirmed by the peaks appearing at 1556 and 1427 cm^{-1} , respectively. The -CH stretching vibration is responsible for the band at 2922 cm^{-1} , while the -CH symmetrical deformation accounts for the band at 1380 cm^{-1} . The glycosidic linkage observed in chitosan is responsible for the absorption peak at 1022 cm^{-1} . The absorption peak at 1060 cm^{-1} may be due to the presence of the C-O stretching band. The stretching vibration of the -OH group is indicated by the distinctive strong broad absorbance band at 3432 cm^{-1} of pure polyvinyl alcohol (PVA), while the symmetric C-H from alkyl groups is represented at 2907 cm^{-1} [41]. The peaks at 1426 and 1093 cm^{-1} are related with the bending vibrations of -OH groups and the stretching vibrations of the C-O groups, respectively. The spectra obtained by the FTIR study of NLE show a stretching band at 3444 cm^{-1} . This may be linked with the -OH stretching vibration of the phenolic group. The FTIR peak obtained due to the presence of NLE can be detected at the 2856 cm^{-1} wavenumber, which is primarily attributed to C-H stretching vibrations. Additionally, the peak at 1636 cm^{-1} corresponds to the C=O stretching of the -COOH group. The FTIR spectrum of the PVA/NLE/CS composite was established due to the shifting of the absorption peaks. From the FTIR spectrum of the PVA/NLE/CS composite, a peak was identified at 3340 cm^{-1} (decreased compared to the individual components). This indicates the reduction of -NH_2 groups after the creation of the required composite material (PVA/NLE/CS). The -COOMe group of azadirachtin present in NLE binds with the -NH_2 groups in chitosan, and this interaction results in the formation of the -NH-CO- bond. A broad and diffuse peak is observed due to the stretching vibration of methylene (-CH_2) present in PVA, which is slightly lowered to 2866 cm^{-1} , perhaps because of stretching vibrations caused by the -C-H bond present in the -CH_3 group. A characteristic peak is recognized at 1552 cm^{-1} , owing to the existence of an amine group in the chitosan molecules of the developed composite film. The peak obtained at 1728 cm^{-1} is due to the stretching vibration of the C=O group in the sample, which confirms the presence of NLE in the composite material. Additionally, a new peak is found at 1027 cm^{-1} (lower frequency), which may be due to the stretching vibration produced by the -C-O bond present in the chitosan and the acetyl group of PVA. This may result from a strong interaction between CS, NLE, and PVA.

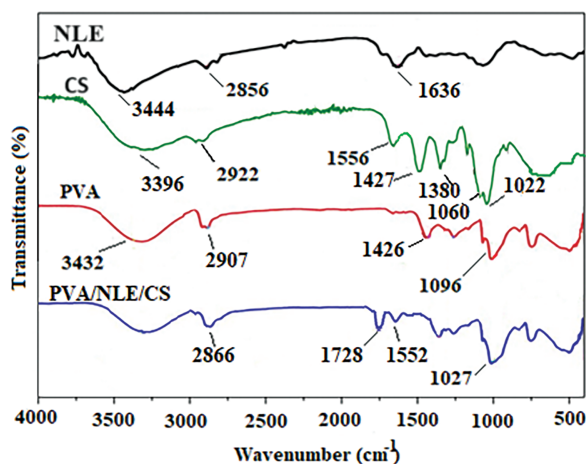


Figure 4: FTIR spectra of PVA, CS, NLE and PVA/NLE/CS composite film

3.3 Thermogravimetric Analysis

The thermal degradation of the extracted chitosan and the synthesized composite film is illustrated in Fig. 5a,b. The TGA analysis of the extracted CS shows two stages of degradation. The first stage is called the weight loss zone, that appears between 50–180°C temperature range, which may be due to the moisture evaporation. The second stage of decomposition was identified between 180°C–490°C temperature ranges, resulting from the breakdown of glycosidic linkages. And the elimination of volatile compounds, also known as the products of combustion [42]. The PVA/NLE/CS composite film exhibits three-stage decomposition. In the first stage, weight loss was observed up to 150°C, which results from the loss of moisture. The second stage, which involves major weight loss that appears within a temperature range of 180°C–350°C, is associated with the deacetylation of chitosan, the degradation of the PVA backbone chain, and the degradation of the hemicellulose and cellulose constituents of NLE. The third and final stage of weight reduction occurs within the temperature range of 350°C–600°C, representing the breakdown of lignin components and the pyrogenic decomposition of unstable residues produced in the second stage, which continues throughout the entire temperature range. The DTG thermograms of the extracted CS and PVA/NLE/CS composite film show the maximum degradation, with the highest degradation occurring at 238°C and 251°C, respectively.

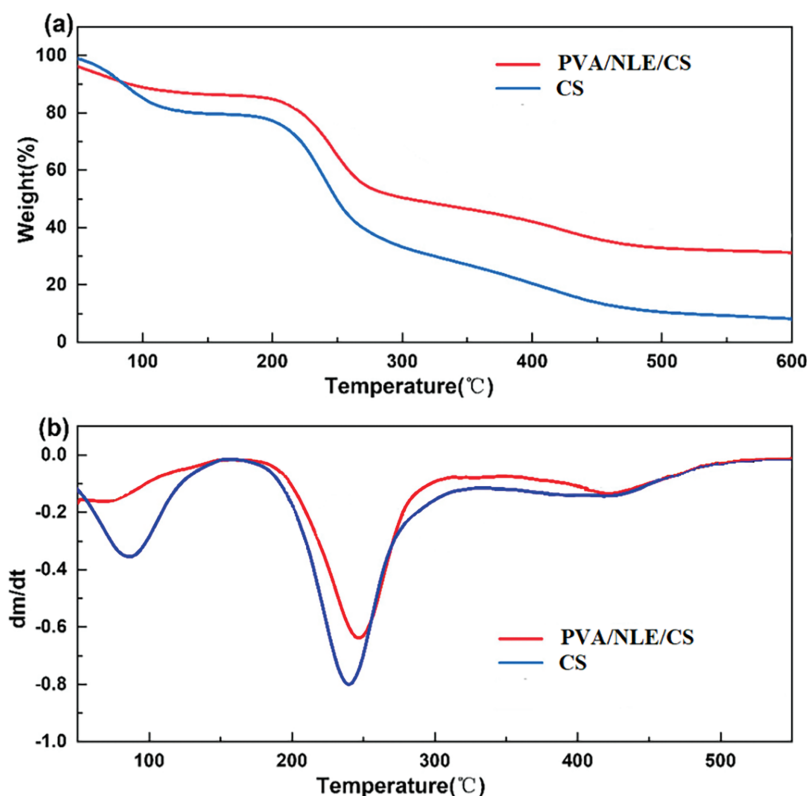


Figure 5: (a) TGA plot of CS and PVA/NLE/CS, (b) DTG plot of CS and PVA/NLE/CS composite film

3.4 SEM-EDX Analysis

The morphological structure and major elemental analysis of the extracted chitosan and PVA/NLE/CS composite film, before and after adsorption of Pb (II) and Cu (II) ions, were determined using SEM-EDX spectral analysis. The SEM images of chitosan illustrated in Fig. 6a indicate that the particles were scattered with a non-homogeneous distribution and porous cavities, exhibiting rough and uneven shapes and sizes.

The elemental analysis of the extracted chitosan indicates the presence of C, O, and N, each with different intensities, that indicates a minimal quantity of protein remnants in the samples. The 'N' value is attributed to the amine ($-\text{NH}_2$) group of chitosan. The morphological appearance of the film (Fig. 6b) shows roughness, irregularity, and unevenness of the surfaces of the film. Hence, the surface of the film appears heterogeneous, containing numerous cavities with an elliptical shape. This may enhance the aggregation of metal ions on the surface of the film. The higher percentage of swelling is due to the presence of these cavities, which are responsible for the hydrophilic nature of the synthesized film of composite material. The EDX analysis of the composite film identifies the elements C, N, and O along with trace amounts of Mg, P, S, K, and Ca, confirming the presence of NLE. After adsorption, the cavities are covered by novel particles (shining), which were not observed in the adsorbent prior to the loading of metals. This may be due to the adsorbate ions. The SEM image of the synthesized material distinctly shows the distribution of metal ions across the surface of the composite adsorbent. This occurs as a result of the development of a single layer of metal ions on the adsorbent surface. From the EDX analysis of these films after adsorption (Fig. 6c,d) of Cu^{2+} and Pb^{2+} ions under non-competitive conditions, it was observed that the elemental components detected in the composite film include C, O, N, Mg, P, S, K, Ca, Cu(II), and Pb(II), which indicate its phase purity and the increasing content of copper and lead. The EDX spectra clearly showed the characteristic peaks corresponding to the presence of metal ions, confirming their adsorption capability.

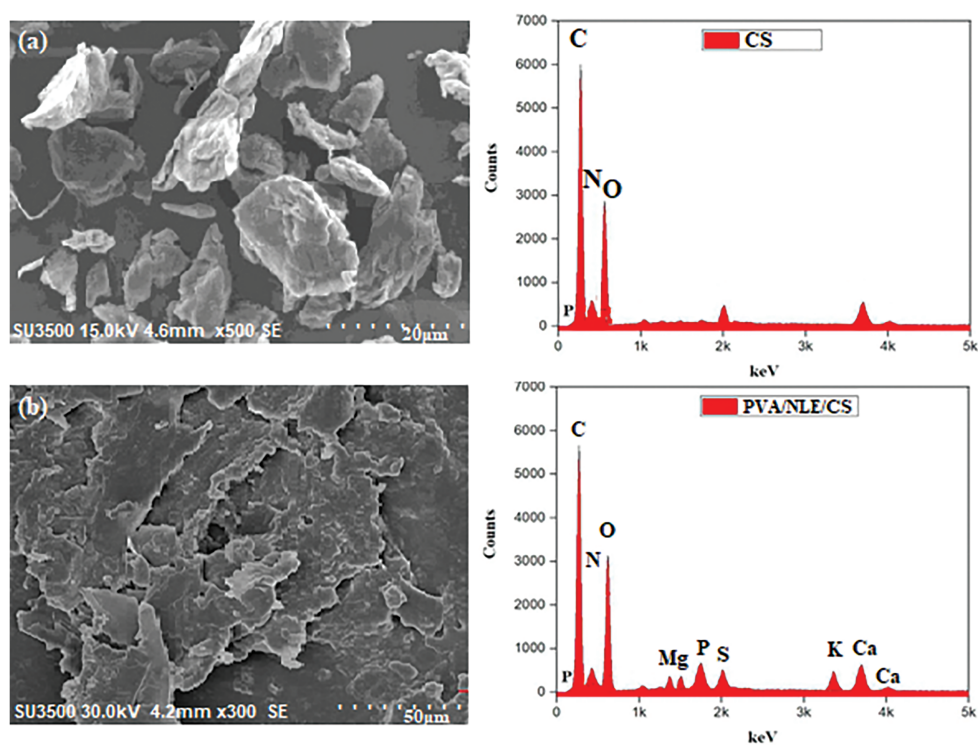


Figure 6: (Continued)

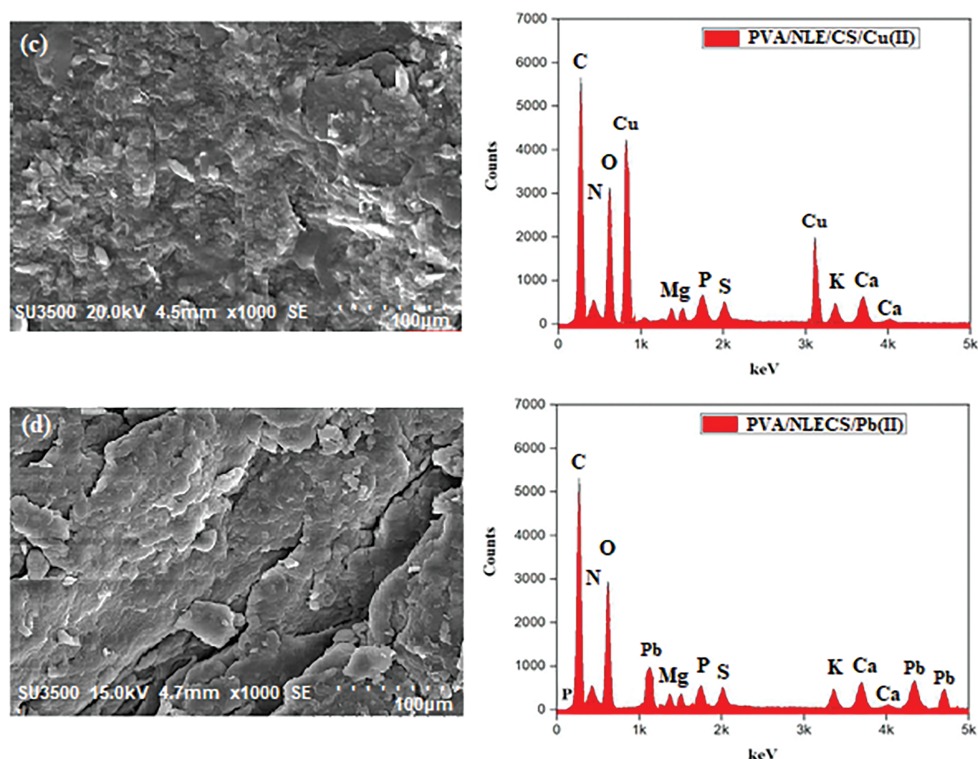


Figure 6: SEM-EDX of (a) extracted chitosan, (b) PVA/NLE/CS composite film before adsorption, (c) PVA/NLE/CS after Cu(II) adsorption, and (d) PVA/NLE/CS after Pb(II) ions adsorption

3.5 X-Ray Diffraction Studies

Fig. 7 highlights the XRD peaks of the extracted CS, PVA, NLE, and PVA/NLE/CS films. The XRD diffractogram of CS indicates major peaks at $2\theta = 10.2^\circ$ and 19.8° , which are attributed to its hydrated crystalline structure [43]. The XRD analysis of PVA evidenced a peak at $2\theta = 19.2^\circ$, which may be due to the semi-crystalline structural aspects of PVA [26]. This occurs because strong hydrogen bonds are formed due to the hydroxyl groups present on the parent chain of the PVA molecule. The amorphous phases in the PVA structure are suggested by the peak at $2\theta = 40.2^\circ$. The XRD pattern of NLE showed 2θ peaks at 11° , 17° , 25° , 33° , 36° , and 45° . The NLE structure is crystalline in nature because of the presence of minerals based on metals, including Ca, Na, Mg, Fe, Cr, Cu, and Zn. A noticeable change was recorded in the XRD patterns, suggesting a noticeable modification in the PVA/NLE/CS films. The shift in 2θ values to $2\theta = 16.2^\circ$ and $2\theta = 24.8^\circ$ in PVA/NLE/CS, when compared to pure CS, NLE, and PVA, indicates structural changes. A significant decrease in intensity is also observed, which can be associated with the presence of broad amorphous peaks, which decrease and confirms molecular miscibility in the polymer matrix.

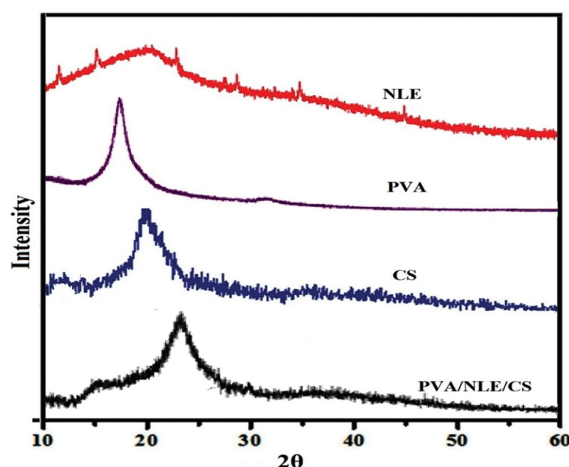


Figure 7: XRD pattern of Chitosan, NLE, PVA and PVA/NLE/CS composite films

3.6 XPS Study

XPS provides the information regarding the chemical state and elemental composition with interaction between the functional groups of PVA, chitosan, and NLE. It confirms the successful adsorption of metals at the surface of the composite material. X-ray photoelectron spectroscopy (XPS) was employed to analyze the interactions between the adsorbent and the adsorbate. Prominent peaks are observed at binding energies of 285, 400, and 531 eV, which correspond to C 1s, N 1s, and O 1s, respectively. As shown in the inset of Fig. 8a, the unmodified sample contains 69.57% carbon, 6.82% nitrogen, and 21.86% oxygen. Similarly, the high-resolution O1s spectrum (Fig. 8b) was divided into three peaks centered at 533.4 eV (O=C=O and O-C-O), 531.9 eV (C-OH), and 531.2 eV (C=O). The high-resolution C1s spectrum (Fig. 8c) was categorized into three distinct peaks at 286.4 eV (representing C-O, C-OH, and C-NH₂), 288.9 eV (corresponding to O-C=O and O-C-O), and 284.8 eV (associated with C-C/C=C/C-H). Due to adsorption, the oxygen content increases to 26.04%, while the carbon content decreased to 65.85%, indicating surface oxidation and the formation of oxygen-containing functional groups like hydroxyl and carboxyl. These groups enhance both adsorption capacity and catalytic performance. The nitrogen content remains stable at approximately 6.8%, suggesting the nitrogen functionalities are structurally stable and contribute to reactivity and adsorption. The integration of oxygen-rich groups facilitates electron transfer, which is essential for effective adsorption and degradation. Binding energy shifts observed after metal ion adsorption indicating that Cu²⁺ and Pb²⁺ ions attach to the hydrogel and composite surfaces. The slight shifts in peak positions further suggest electrostatic interactions between the metal ions in solution and the oxygen atoms in the composite [44].

3.7 Swelling (%)

The synthesized composite material exhibits significant swelling behaviour due to the hydrophilic properties of PVA and the existence of numerous pores and voids on the surface layer, which result from the cross-linking of polymer chains of the synthesized composite material [45]. The swelling behaviour of the developed PVA/NLE/CS composite film was studied over different time intervals using distilled water. The hydrophobicity of the material appears due to the -OH groups present in carboxylic acids, which possess an exceptional capacity to form hydrogen bonds on interaction with molecules of water. This is the cause of increase in the capability of absorbing water. At the time of synthesis of the composite material, the formation of hydrogen bonds between the PVA and chitosan molecules increases the cross-linking; therefore, the penetration of water increases, resulting in the increase in swelling ratio. But after 80 min the NLE

decreases the rate of water vapor transmission or film solubility. The decrease in solubility reduces the absorption of water by the composite film over time, resulting in the decrease in swelling ratio [46]. The developed novel composite film material possesses excellent water absorption capability and, therefore can be used successfully for cultivation and gardening in water-scarce or desert areas. Fig. 9 illustrates the swelling capability of the PVA/NLE/CS composite films.

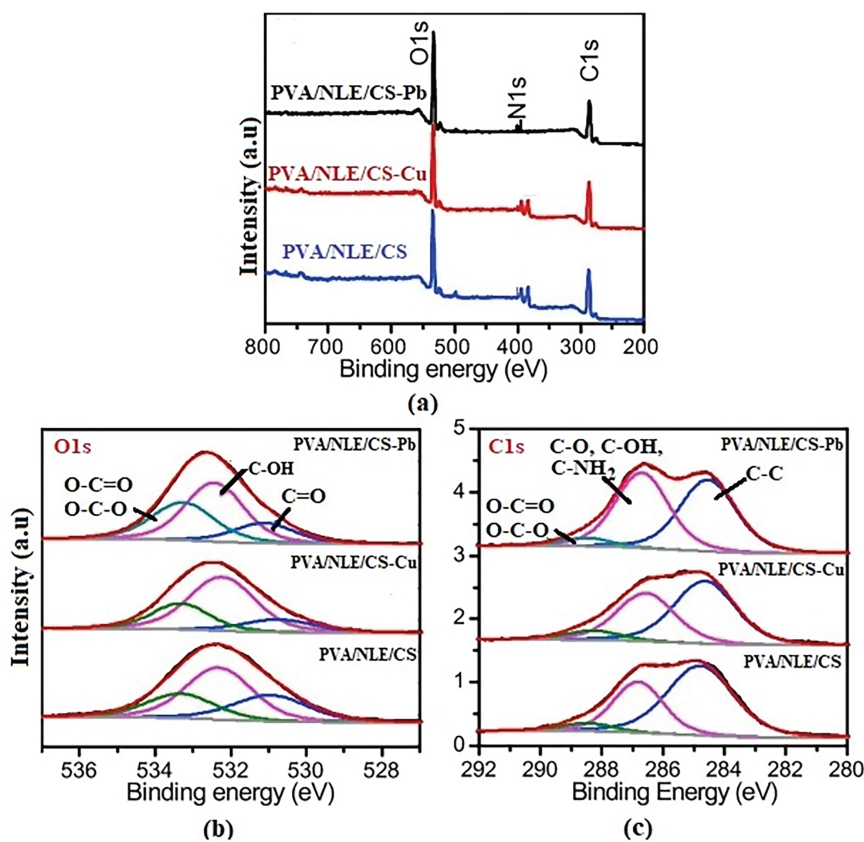


Figure 8: XPS spectra of PVA/NLE/CS (a) survey spectrum before and after adsorption, (b) O 1 s spectrum, (c) C 1 s spectrum

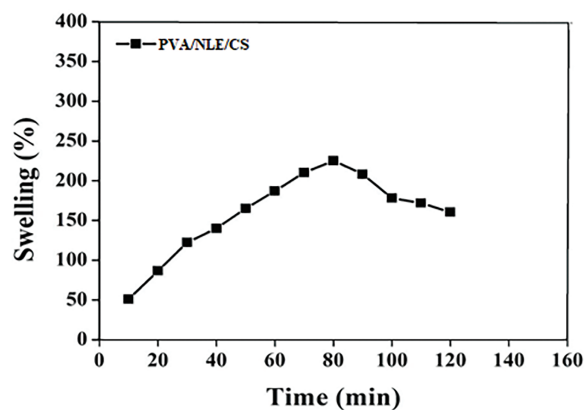


Figure 9: Swelling graph of PVA/NLE/CS composite film

3.8 Antibacterial Activity

The bacteriological activity of the synthesized biomaterial film for both bacteria (*E. coli* and *S. aureus*) has been analyzed using the agar plate method. The results obtained revealed that PVA/NLE/CS possesses potential antibacterial activity against both bacteria. The antibacterial activity of PVA/NLE/CS is perhaps due to the biocidal action of each constituent. The antibacterial activity can be explained due to the presence of positively charged amino groups ($-NH_2$) present in chitosan molecules. The phenolic $-OH$ groups in PVA and NLE are directly linked with the phospholipid cell membrane [47]. This leads to seepage of intracellular constituents and destruction of bacterial cells. The calculated zone of inhibition and the activity index are illustrated in Table 2. Fig. 10 shows the antibacterial activity of PVA/NLE/CS composite films.

Table 2: Zone of inhibition and the activity index of the composite film

Samples	<i>E. coli</i>		<i>S. aureus</i>	
	Zone (mm)	Activity	Zone (mm)	Activity
PVA/NLE/CS	16	76.19	18	60
Ampicillin	21	100	30	100

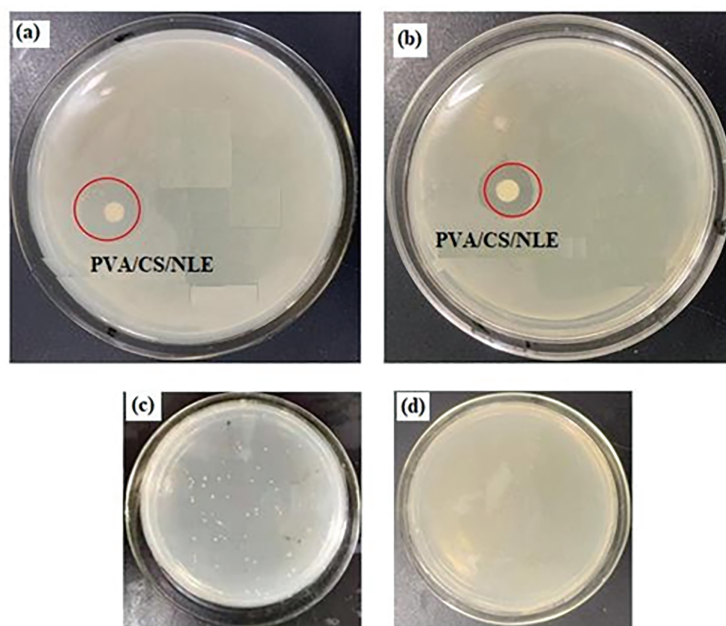


Figure 10: PVA/NLE/CS composite films in (a) *E. coli* bacteriostatic zone (b) *S. aureus* inhibition zone, (c) PVA/NLE/CS film inhibition zone in *E. coli* and (d) PVA/NLE/CS film inhibition zone in *S. aureus*

3.9 Adsorption Mechanism

Fig. 11 illustrates the proposed mechanism for the adsorption of Cu^{2+} and Pb^{2+} onto the PVA/NLE/CS composite. The adsorption of these metal ions from aqueous solutions primarily occurs through interactions between the hydroxyl ($-OH$) and amino ($-NH_2$) functional groups of chitosan present in the composite material. Following the adsorption of Cu^{2+} and Pb^{2+} , a precipitate forms, and the metal ion concentration within this precipitate reflects the adsorption efficiency. More number of active sites specifically the hydroxyl and amino groups present on the surface of the composite material significantly enhances the adsorption

process [48]. The adsorption process is facilitated by the combination of electrostatic attraction, chelation, and ion exchange technique. Due to the protonation and deprotonation of numerous amino groups on the surface of composite, strong binding created between the nitrogen atoms of the amino groups and the metal ions, increasing rate of adsorption. SEM images recorded before and after metal ion adsorption demonstrate the effectiveness of the composite. The microporous structure increases the accessibility of functional groups, providing a large number of active sites that promote the efficient chemisorption of Cu^{2+} and Pb^{2+} ions. Although electrostatic repulsion between Cu^{2+} and Pb^{2+} cations hinders the adsorption process, but its effect is minimal [49].

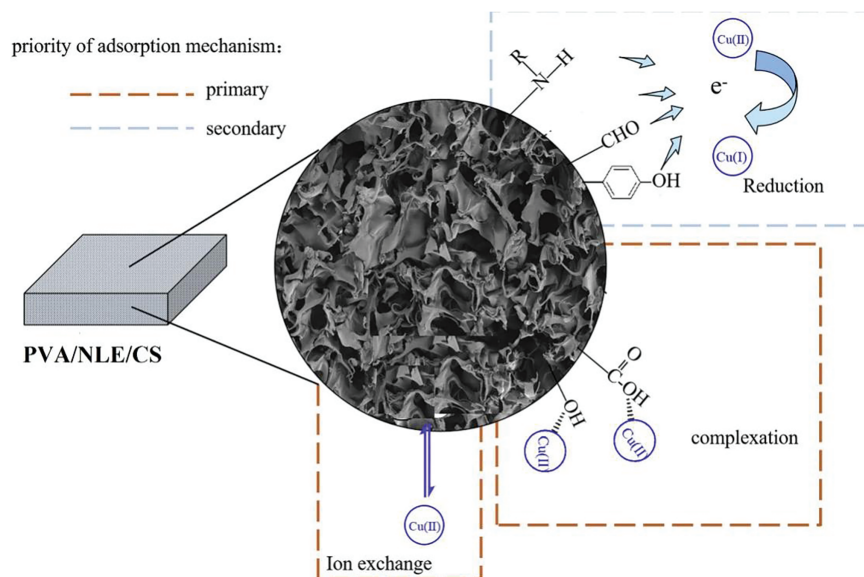


Figure 11: Schematic representation of mechanism of adsorption of Cu^{2+} and Pb^{2+} ions

The large number of functional groups [carboxyl ($-\text{COOH}$) and hydroxyl ($-\text{OH}$)] present in NLE serves as active binding sites for the removal of metal ions (Cu^{2+} and Pb^{2+}). The mechanism of adsorption of toxic metals through the composite based on NLE basically involves physical adsorption at the surface because of the formation of a complex due to electrostatic interactions between the targeted metals and functional groups present in the composite material, and facilitates the removal of metals. The various factors that influence the rate of adsorption include the nature of the metals present in the water sample, pH, temperature, and surface of the composite material. The physical adsorption mainly occurs due to electrostatic interactions and van der Waals forces [50].

3.10 Adsorption–Desorption Cycle

NLE is used as a good biosorbent, which functions in adsorption–desorption cycles, and this shows the stability and reusability of the adsorbent material. It functions with long-term adsorption capability and recyclability for the removal of heavy metals and is used in multiple cycles. NLE establishes excellent reusability in adsorption–desorption cycles for removing the contaminants from wastewater and exhibits capacity retention over multiple cycles, but a gradual decrease in efficiency is observed. The capacity retention mainly depends on the kinds of heavy metals present in the water sample and the conditions of the desorption method used. NLE maintains structural stability because of its porous structural network and permits the adsorption of Cu^{2+} and Pb^{2+} with high removal efficiency. NLE serves as an excellent biosorbent, reusable in a number of adsorption-desorption cycles, but the leaching is restricted. Since leaching is less, therefore

deactivation of the number of active sites during adsorption in each cycle is less, which results in long-term reusability of NLE [51,52].

3.11 Results of Elimination of Metal Ions

The adsorption parameters of Cu^{2+} and Pb^{2+} and their corresponding ions can be effectively optimized by considering parameters obtained from experiments, including contact time, pH before and adsorption, the initial concentration of the adsorbent, and the temperature of the experimental conditions. The pathway of adsorption was studied using a suitable methodology.

3.11.1 Effect of Adsorbent Dosage

The impact of adsorbent dosage on the adsorption of Cu^{2+} and Pb^{2+} ions onto the adsorbent surface at a specific pH (pH 6) and temperature (27°C) was evaluated using varying amounts of PVA/NLE/CS composite films. The range of the adsorbent dosage selected was 0.1–0.6 g, and the percentage of adsorption of the metal ion was noted. This could be attributed to a greater number of binding sites and an expanded surface area of the adsorbent, leading to enhanced ion removal from the solution. Over time, the adsorption rate declined as the adsorbent material reached saturation due to the addition of an optimal amount of adsorbent. The adsorption percentages varied with different adsorbent dosages, demonstrating that the adsorption tendency of PVA/NLE/CS films improves with an increase in adsorbent dosage, following the trend $\text{Cu}^{2+} > \text{Pb}^{2+}$. Fig. 12a,b depicts the effect of varying adsorbent dosage on the adsorption efficiency of the PVA/NLE/CS films for metal ions.

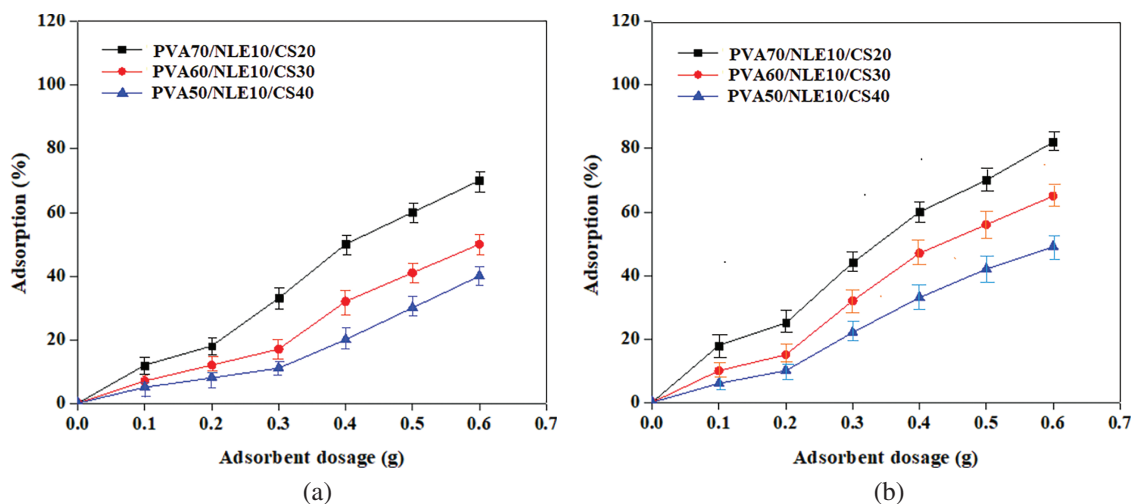


Figure 12: (a) Effect of adsorbent dosage on Cu^{2+} adsorption. (b) Effect of adsorbent dosage on Pb^{2+} adsorption

3.11.2 Effect of pH on Adsorption

Each adsorption method is affected by pH, similar to the interaction between various metal ions and adsorbent sites. The results indicate that the adsorption efficiency depends on both pH and temperature. In this study, 0.1 g of the synthesized composite material was introduced into a 70 mg/L solution of toxic metal ions, with the pH maintained between 2 and 8. At lower pH levels, the capability of adsorption of metal ions (Cu^{2+} and Pb^{2+}) is reduced because the $-\text{NH}_2$ amino groups in CS become protonated to $-\text{NH}_3^+$, which repels other positively charged ions like Cu^{2+} and Pb^{2+} , thereby lowering the adsorption rate [53]. However, adsorption capacity improves as pH increases within 3 to 6.

The presence of the functional groups such as carboxyl (-COOH) and hydroxyl (-OH) groups present in the composite material act as the primary adsorption sites for metal ions, even in an acidic medium. Under low pH, many active functional groups undergo protonation, with the rate increasing up to pH 6 before decreasing due to competitive adsorption. At pH levels above 6, the adsorbent surface gains more negative charge due to deprotonation, reducing competition with metal ions for binding sites and increases the adsorption capacity. Fig. 13a,b illustrates the impact of pH on the adsorption rate.

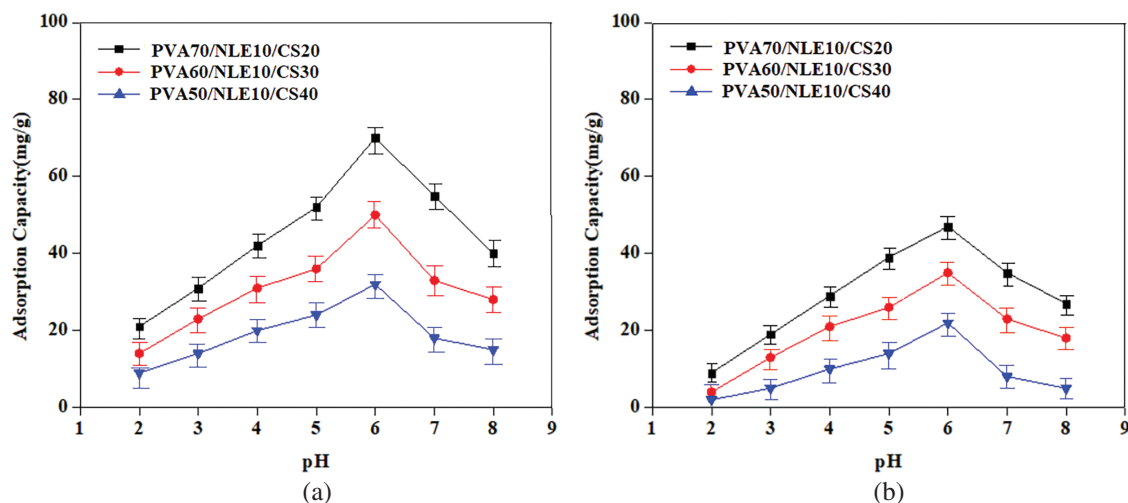


Figure 13: (a) Plot of effect of pH on adsorption of Cu^{2+} ions; (b) Plot of effect of pH on adsorption of Pb^{2+} ions

3.11.3 Effect of Contact Time

The impact of contact time on the uptake of metal ions depends on the concentration of the ions and the properties of the synthesized composite film. Fig. 14a,b represents the effect of contact time on the adsorption capability of Pb^{2+} and Cu^{2+} ions. The experimental results indicate that the adsorption capability progressively improves with increase in contact time and reaches maximum at 180 min. After that, it stabilizes, and equilibrium is attained for both targeted metal ions. The adsorption capability follows the order $\text{Cu}^{2+} > \text{Pb}^{2+}$, and after a certain period of contact, the adsorption efficiency remains constant. The higher adsorption rate at the initial stage is perhaps owing to the formation of more unoccupied active sites on the adsorbent (composite) surface, with time these sites gradually decrease [54]. The adsorption equilibrium might be observed due to Pb^{2+} and Cu^{2+} ions occupying the vacant sites on the adsorbent surface, which restricts the mass transfer of metal ions from the aqueous solution to the outer surface of the adsorbent.

3.12 Isotherm Studies

The adsorption isotherm illustrates the interaction of different metal ions attached to the adsorbent material, which is still present in the aqueous solution. This is a crucial parameter required for the process of adsorption. In this research work, the Langmuir and Freundlich isotherm models were both applied for analysing the experimental result and designed a theoretical adsorption system for removing metal ions from the solution. Among these, the Langmuir monolayer adsorption model is better and most extensively applied isotherm and is expressed using Eq. (4).

$$\frac{c_e}{Q_e} = \frac{1}{b \cdot Q_{\max}} + \frac{c_e}{Q_{\max}} \quad (4)$$

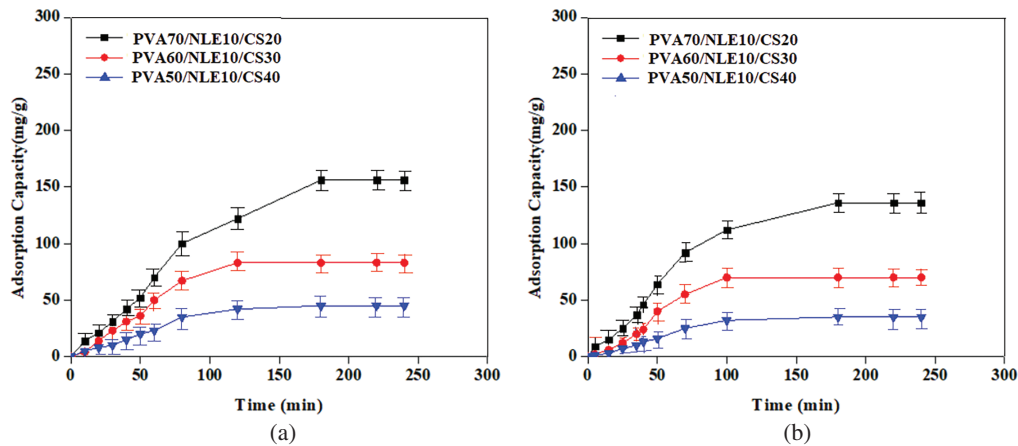


Figure 14: (a) Effect of contact time on Cu^{2+} ions adsorption; (b) Effect of contact time on Pb^{2+} ions adsorption

In the given expression, “b” indicates the adsorption free energy (L/mg), while Q_{max} represents the highest monolayer adsorption capability according to the Langmuir model, measured in mg/g. C_e indicates the initial concentration (mg/L), and Q_e refers to the adsorption capacity (mg/g). The values of “b” and Q_{max} are measured using the intercept and slope of the Langmuir adsorption plot, where C_e is plotted against C_e/Q_e . Furthermore, R_L is a crucial parameter in the Langmuir isotherm [55]. It is defined and interpreted using Eq. (5).

$$R_L = \frac{1}{(1 + bc_0)} \quad (5)$$

C_0 (mg/L) represents the concentration of metal ions prior to adsorption, whereas the value of R_L reflects the viability of the isotherm. An R_L value ranging from 0 to 1 confirms favourable and viable adsorption, whereas $R_L = 1$ shows unfavourable adsorption with linear adsorption behaviour. The plots based on the linear isotherm based on the Langmuir model of PVA/NLE/CS are presented in Fig. 15a. The adsorption ability of Pb^{2+} and Cu^{2+} metal ions onto PVA/NLE/CS was closely aligned with the Langmuir equation ($R_L = 0.9$), signifying the creation of a single molecular layer of metal ions on the surface of the adsorbent at saturation stage.

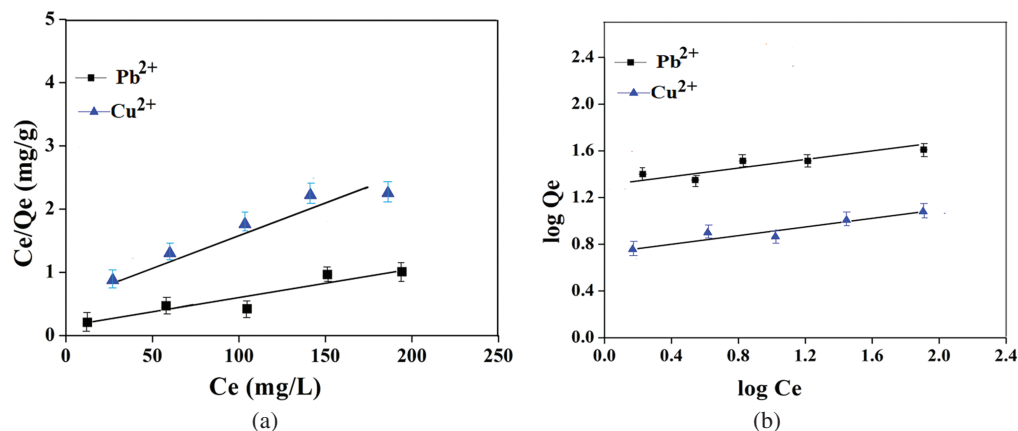


Figure 15: (a) The linear isotherms plot of Langmuir model PVA/NLE/CS. (b) The linear isotherms plot of Freundlich model PVA/NLE/CS

The Freundlich model explains heterogeneous nature of adsorption by considering the various sites for adsorption found in the material (hydrogel) and the diversity of metal ions undergoing adsorption. The heterogeneity factor ($1/n$) characterizes the behaviour of hydrolysed or free species. The linear state of the Freundlich equation is represented in Eq. (6).

$$\log Q_e = \log k_f + 1/n \log C_e \quad (6)$$

C_e refers to the equilibrium concentration in mg/L, while k_f plays an approximate indicator based on capacity (Freundlich isotherm). The parameter 'n' denotes the number of functional active sites in the composite material, which is accountable for the adsorption of metal ions [56].

The study revealed that the Freundlich isotherm model had achieved the highest R^2 value, indicating a superior fit for the adsorption data. $1/n < 1$, indicates favourable and heterogeneous adsorption. Accordingly, the $1/n$ values demonstrated the favourability of metal ion adsorption onto the surface of the PVA/NLE/CS composite film. This study revealed that Pb^{2+} exhibited a relatively lower adsorption capacity than Cu^{2+} . The 'n' value for each kind of metal ion is found to be greater than one, indicating effective adsorption of metal ions, which is validated by the correlation coefficient (R^2), where $R^2 > 0.99$ (Fig. 15b).

Since $R^2 > 0.99$ (Table 3), it demonstrated that both the metal ions are effectively adsorbed by the composite film. This experimental data is compared with the results of the Freundlich and Langmuir isotherms. But from these two models, the Langmuir isotherm kinetic model is more effective as compared to the Freundlich isotherm. It is suggested that the Langmuir isotherm model more accurately predicts the adsorption of Cu^{2+} and Pb^{2+} metal ions from solution.

Table 3: Freundlich and Langmuir isotherms of various metal ions through PVA/NLE/CS composite films

Metal ions	PVA//NLE/CS					
	Langmuir		Freundlich			
	Q_{max} (mg/g)	b (L/g)	R^2	n	k_f	R^2
Cu^{2+}	11.23	0.037	0.9944	1.01	2.66	0.9309
Pb^{2+}	34.12	0.021	0.9943	2.4	17.30	0.9968

3.13 Kinetics

Hence, adsorption kinetics is essential for determining the time required for the uptake of Cu^{2+} ions on the adsorbent surface and for interpreting the transport mechanism. The adsorption kinetics behaviour of both metal ions was assessed using typical theoretical models, which provide useful information for modelling. The adsorption kinetics of the result was studied based on pseudo-second-order and pseudo-first-order kinetic models. Furthermore, the intra-particle diffusion kinetics model was employed to examine diffusion mechanisms [50–52]. The mathematical formulas for these three kinetic models, i.e., pseudo first-order, pseudo second-order, and intra-particle diffusion kinetics model, are represented in Eqs. (7)–(9), respectively.

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (7)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (8)$$

$$Q_t = k_i t^{1/2} + C \quad (9)$$

Q_e and Q_t represent the amounts of ions adsorbed onto the adsorbents (mg g^{-1}) at the stage of equilibrium and at a given time in min. For pseudo-first-order adsorption kinetics the rate constant is k_1 (min^{-1}), whereas for pseudo-second-order adsorption kinetics, the rate constant is k_2 ($\text{g mg}^{-1} \text{min}^{-1}$). The rate constant for intra-particle diffusion adsorption kinetics is represented by k_i ($\text{mol g}^{-1} \text{min}^{-1/2}$), while C is a constant expressed in moles per gram (mol/g). Table 4 illustrates the kinetic models based on intra-particle diffusion, pseudo-first-order, and pseudo-second-order adsorption.

Table 4: Comparison parameters of kinetic models for the Pb^{2+} and Cu^{2+} adsorption

Kinetic model	Parameter	Cu^{2+}	Pb^{2+}
Pseudo-first-order	Q_e (mg/g)	384	798
	Q_t (mg/g)	413	12.3
	K_1 (min^{-1})	7.4×10^{-4}	0.037
	R^2	0.912	0.932
Pseudo-second-order	Q_t (mg/g)	402	831
	K_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	1.1×10^{-5}	2.86×10
	R^2	0.996	0.990
Intra-particle diffusion	Q_t (mg/g)	316	876
	K_i ($\text{mg g}^{-1} \text{min}^{-1}$)	19.64×10^{-2}	11.19
	C (mg/g)	-14.42	-7.44
	R^2	0.868	0.842

The analysis of this model revealed that the pseudo-first-order kinetic model is not appropriate for defining the adsorption of Cu^{2+} and Pb^{2+} on the surface of the composite, as evidenced by its low correlation coefficient. In contrast, the pseudo-second-order kinetic model shows comparatively more accuracy of the adsorption kinetics of the specific metal ions (Fig. 16). The adsorption capacity (Q_e) predicted by this model closely aligns with the experimentally determined values (Q_t). Furthermore, the intra-particle diffusion model exhibits a lower correlation coefficient compared to both the pseudo-first-order kinetic model and pseudo-second-order kinetic models, suggesting that it is not an appropriate model for describing the adsorption process of Pb^{2+} and Cu^{2+} onto the surface of the composite.

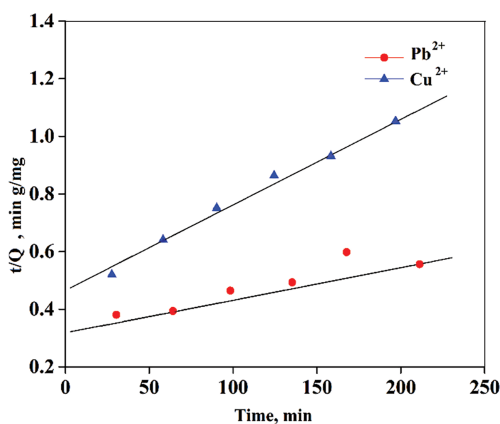


Figure 16: Kinetic plot of adsorption for Cu^{2+} and Pb^{2+} by pseudo-second-order model

4 Conclusion

This study highlights the development of an innovative PVA/NLE/CS composite films synthesized under optimal conditions using a sustainable, cost-effective solvent casting method. The fabricated composite films were analyzed using FTIR, TGA-DTG, SEM-EDX, and XRD techniques. FTIR analysis confirmed the formation of strong bonds among CS, PVA, and NLE components. Morphological study indicates that the composite possesses numerous active sites, attributed to the presence of hydroxyl (-OH) and amino (-NH₂) groups, which are responsible for an increase in the capability of adsorption of Cu²⁺ and Pb²⁺ ions. Antibacterial study demonstrated that the composite film creates inhibition zones against both *E. coli* and *S. aureus*, bacteria, indicating its potential to prevent bacterial penetration. At pH 6, the adsorption capacity of the composite material increases steadily with higher adsorbent dosage, reaching its peak at 0.6 g. Maximum adsorption efficiency is observed at 180 min. Competitive adsorption studies revealed that the individual adsorption capacities for Cu²⁺ (61.5 mg/g) and Pb²⁺ (52.08 mg/g) are higher compared to their capacities under competitive conditions (Cu²⁺ at 37.1 mg/g mg/g and Pb²⁺ at 31.35 mg/g). Computational modelling and machine learning technique can assist in tailoring and designing that improves the performance of adsorption and practical application. These findings underscore the strong potential of the composite material for removing toxic metals from contaminated water, which is suitable for wastewater treatment. However, challenges such as material loss during adsorption, limited adsorption capacity, low selectivity, and difficulties in regeneration and reuse remain key limitations for this material.

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Availability of Data and Materials: The authors confirm that the data supporting the findings of this study are available within the article.

Ethics Approval: Not applicable.

Conflicts of Interest: The authors declare no conflicts of interest to report regarding the present study.

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