Biosorption of Cadmium(II) and Copper(II) ions using Kneaf fiber cellulose/Carbon nanotubes/Polyethylene glycol ternary blend

S.M. Ameenur Rahman¹, T.N. Balaji¹, T. Gomathi², P.N. Sudha² and A.K.S. Ibrahim Sheriff¹*

¹PG and Research Department of Chemistry, C. Abdul Hakeem College (Autonomous), Melvisharam, Affiliated to Thiruvalluvar University, Tamil Nadu, India
²Biomaterials Research Lab, D.K.M. College for Women (Autonomous), Vellore, Affiliated to Thiruvalluvar University, Tamil Nadu, India

(*Corresponding author Email: isisis_1@yahoo.co.in (Ibrahim Sheriff); drparsu8@gmail.com (P.N. Sudha); drgoms1@gmail.com (T. Gomathi))

Abstract
The goal of this study was to make Kneaf fibre cellulose (KFC), Carbon nanotubes (CNT), and Polyethylene glycol (PEG) with and without glutaraldehyde crosslinker to remove the hazardous heavy metals copper and cadmium. FTIR, XRD, and SEM analyses were used to characterise the produced ternary blends. Based on XRD and SEM results, the amorphous form of the KFC/CNT/PVA + Glu ternary blend confirmed its suitability for the removal of Cd(II) and Cu(II) ions. Batch adsorption studies are performed to test the adsorption effectiveness of a material by varying parameters such as adsorbent dose, contact time, pH, and beginning metal ion concentration. Pseudo-first-order and pseudo-second-order models were used to analyse the data, which were then fitted to Langmuir and Freundlich isotherms. The findings show that the Freundlich equation and pseudo-second-order kinetic models can be stated more accurately. Under ideal conditions, the KFC/CNT/PVA + Glu ternary blend was observed to remove Cu(II) ions more effectively than Cd(II) ions.

Keywords: Kneaf fibre based cellulose blends, Cu(II) and Cd(II) ions, Batch adsorption studies.

Introduction
Water is the most valuable natural resource on the planet, as life on the planet would be impossible without it [1]. Due to protracted droughts (climate change), population increase, significant industrialization, and poor disposal, the world is experiencing a difficulty in satisfying rising needs for unpolluted water [2]. Each year, the industrial sector is predicted to dump 300-400 million tonnes of heavy metals, solvents, toxic sludge, and other trash into water sources around the world [3].

Among the contaminants, heavy metal ions are one of the world's most serious environmental pollutant, because of the creation of complex chemicals within the cell, these can be hazardous to all kinds of life. Once introduced into the ecosystem, they cannot be biodegraded. Copper and cadmium are highly poisonous heavy metals that are widely found in industrial workplaces and are causing widespread concern from both an environmental and economic standpoint due to their severe impact on humans, flora, and fauna [4].
Removal of heavy metals using biomaterials has been recognised as a potential method [5]. The two main advantages of biosorption technology is its efficiency in decreasing heavy metal ion concentrations to very low levels, as well as the utilisation of inexpensive biosorbent materials. Kenaf is a well-known cellulosic feedstock that offers both economic and environmental benefits. A fiber's layers are made up of cellulose embedded in a hemicellulose and lignin matrix. Cellulose polymer was negatively charged, because it possesses many carboxyl and hydroxyl groups [6]. Hydrogen bonding between two neighbouring polymer chains is possible thanks to the hydroxyl groups in cellulose. The most significant disadvantage of cellulose was its low density and poor mechanical qualities. Carbon nanotubes and polyvinyl alcohol were added to improve the characteristics of kenaf fibre cellulose in the presence of the crosslinker glutaraldehyde.

CNTs have been researched for the removal of toxic contaminants in the last several decades, and their performance has been compared to other carbon-based adsorbents utilised in application areas [7–9]. PEG was non-toxic and biocompatible material. Because of its larger specific surface area and adsorption capability, activated carbon (AC) is frequently utilised as an adsorbent [9,10]. The polymer chains gained mechanical and chemical strength as a result of the chemical reaction within the network. The most common way for improving these qualities was chemical crosslinking, which transformed the polymeric structure into a three-dimensional network.

Thus the present work aimed to prepare the new adsorbent by mixing KFC, CNT and PVA in the absence and presence of glutaraldehyde crosslinker. It was characterized and used to investigate the adsorption efficiency of Cu(II) and Cd(II) ions. The efficiency of the material towards heavy metal removal was estimated through batch adsorption mode.

Materials and methods

Materials
Vibrant Nature in Chennai provided the kenaf (Hibiscus cannabinus) fibre. Nanobeach in New Delhi provided a multiwalled carbon nanotube (outer diameter 20 nm, inner diameter 5 nm, number of walls 5-15, length 50 m). Himedia Laboratories Pvt. Ltd., Mumbai, provided the polyvinyl alcohol. Nice Chemicals Private Limited, Cochin, provided analytical grade cadmium carbonate, and Central Drug House Pvt. Ltd., New Delhi, provided analytical grade copper sulphate, both of which were utilised as received.

Preparation of kenaf fiber cellulose/ carbon nanotubes/ polyethylene glycol ternary blend
In the absence of glutaraldehyde crosslinker, 1 g of prepared KFC, 0.2 g of CNT, and 1 g of PVA dissolved/dispersed in water separately were taken and blended under magnetic stirring for about an hour at room temperature to obtain KFC/CNT/PVA ternary blend. To make the crosslinked ternary mix, repeat the method with the addition of 7 mL glutaraldehyde. The created ternary blend solution was then placed into a petri dish and allowed to dry.

Characterization
The Shimadzu IRAffinity-1S spectrometer was used to collect FTIR spectra with wavenumbers ranging from 4000 to 400 cm⁻¹. The crystalline nature of the sample was investigated using a Shimadzu XD – D1 powder XRD. The JEOL JSM – 6390LV was used to evaluate surface morphology at a voltage of 20 kV.
Batch adsorption studies

Batch adsorption tests were conducted to determine the ability of the KFC/CNT/PEG blend as adsorbents to remove cadmium (II) and copper (II) from aqueous solution. Changing the pH (4 to 8), adsorbent dosage (1 g to 6 g), contact time (60 to 480 min) and initial metal ion concentration (1000 mg/L to 50 mg/L) the best conditions for metal biosorption can be determined. Using AAS results, the concentration of Cu(II) and Cd(II) ions remaining in solution was determined, and metal ion removal percentage was estimated using the formula below.

\[
\text{Removal} \, (\%) = \frac{C_o - C_f}{C_o} \times 100
\]

where \(C_o\) - Initial concentration of metal ion (mg/L) and \(C_f\) - Final concentration of metal ion (mg/L).

Results and Discussion

FTIR studies

![FTIR spectrum of KFC/CNT/PEG ternary blend](image)

**Figure 1: FTIR spectrum of KFC/CNT/PEG ternary blend**

FTIR spectra of KFC/CNT/PEG ternary blend in the absence and presence of glutaraldehyde are illustrated in Figure 1 and 2. In the FT-IR spectrum of KFC/CNT/PEG ternary blend prepared in the presence and absence of crosslinker show a broad band at 3388 and 3386 cm\(^{-1}\) indicates the stretching vibration of OH and COOH functional groups. The broadness of the band is due to the formation of inter and intra molecular hydrogen bonding [11]. The prominent bands of KFC/CNT/PEG ternary blend (Figure 1) at around 2945, 2875, 1645, 1495, 1430, 1038 cm\(^{-1}\) are assigned to the asymmetric and symmetric stretching of CH group, C=O group, C=C group, stretching vibrations of carboxylic and carboxylate groups, C-O-C linkage respectively [12,13].

In the spectrum of KFC/CNT/PEG + glu blend, two vibrational bands observed between 2954 and 2924 cm\(^{-1}\) is due to C-H stretching modes of vibration. While adding the crosslinker the considerable shift the vibrational bands were taken place. The band at 1645
cm$^{-1}$ for C=O and C=C was shifted to 1639 cm$^{-1}$. This decrease in frequency indicates the effective participation of these functional groups in covalent and non-covalent interactions. The change in band intensity and shift in wavelength observed when comparing the ternary KFC/CNT/PVA blends in the absence and presence of crosslinker validates the blending and crosslinking of the polymer blends [14].

![Figure 2: FTIR spectrum of KFC/CNT/PEG + Glu ternary blend](image)

**XRD studies**

![Figure 3: XRD pattern of KFC/CNT/PEG ternary blend](image)
The most adaptable and commonly used method of characterising materials of all types is X-ray diffraction [15]. This methodology is the most precise and reliable analytical method for determining skeleton structures in semi-crystalline polymers such as thermoplastics, thermoplastic elastomers, and liquid crystalline polymers [16]. X-ray diffraction was used to analyse the structure and crystalline character of the ternary blends generated (Figure 3 and 4). Typical peaks at $2\theta = 18^\circ$ and $22^\circ$ (XRD pattern not specified) and a degree of crystallinity of 73.52% illustrate the crystalline nature of pure cellulose. The intramolecular hydrogen bonding of cellulose was connected to a higher degree of crystallinity. When this KFC is combined with CNT and PEG in the presence of a crosslinker, hydrogen bonds are broken in the crystalline region of the cellulose chain, leading in a loss in crystallinity. Furthermore, PEG is water soluble, causing crystalline structural deformation.

The presence of functional groups such as OH, COOH, C=O, C-O-C, and C=C were involved in covalent and non covalent interactions as a result of adsorption, and that crystallinity development within a polymer is dependent on its structural regularity, with polarity, the presence of hydrogen links, and the capacity to polymer chains among the influencing factors. As a result, metal ion adsorption onto the KFC/CNT/PEG + Glu ternary blend was observed to be successful.

**SEM analysis**

The SEM image shows that the blend KFC/CNT/PEG + glu (Figure 5b) had rough surface with a greater number of uneven loose spherical domains when compared to without crosslink agent (Figure 5a). It is observed that a uniform and smooth surface morphology is found in the case of the PEG blend with a KFC and CNT. While adding the crosslinking agent to KFC/CNT/PEG blend, the morphology and average diameter distribution of the KFC was altered with rod-shaped fibrils on the surface. The homogeneity of the material was also observed from the SEM images through hydrogen bonding between -OH and -C=O groups [17].

![XRD pattern of KFC/CNT/PEG + glu ternary blend](image-url)
Batch adsorption studies

Effect of pH

Ionisation and speciation of heavy metals are affected by solution pH, which is a regulating factor in metal ion removal from water. Equilibrium sorption studies at various pH levels were used to investigate the effect of the suspending medium's pH on metal removal. The metal concentration (200 ppm), amount of KFC/CNT/PEG + Glu blend (1g), contact period (1 h), and temperature (30°C) were all kept constant during this process. Copper and cadmium sample solutions were obtained and placed in measuring flasks. Each sample solution received 1 g of KFC/CNT/PEG + Glu blend, and the pH was changed from 4 to 9. For one hour, flasks were stirred on an orbital shaker (top loaded). The solutions were then filtered, and the filtrates were tested for Cu(II) and Cd(II) ions concentration using atomic absorption spectrum analysis.
The result (Figure 6) shows that adsorption increases when the pH of the metal ion solution rises from 4 to 5 in the case of Cu(II) and Cd(II), but then drops. The pH at which Cu(II) and Cd(II) ions can be removed was discovered to be 5. Cu(II) and Cd(II) ions were removed to a maximum of 92% and 85% of their original concentrations, respectively. The concentration of hydronium ions (H₃O⁺) is enhanced at low pH due to the presence of a higher amount of H⁺ ion. This scenario will result in competition between H₃O⁺ ions and metal ions for available active binding sites on the surface of biosorbents [14,15,18], resulting in a decrease in metal ion removal.

**Effect of adsorbent dose**

The adsorbent capacity towards the adsorbate was determined by the varying the adsorbent dose. By adjusting the amount of KFC/CNT/PEG + Glu blend in aqueous solutions from 1 g to 6 g/l while maintaining other parameters (pH and contact duration) constant, the effect of adsorbent dosage on Cu(II) and Cd(II) ions removal from aqueous solutions was investigated (Figure 7). It was discovered that raising the adsorbent's dosage from 1 g to 6 g improved the adsorbent's removal effectiveness in general. This is owing to the fact that the larger the doses of adsorbents in the solution, the more exchangeable sites for the ions are available. At a dosage of 6 g, the greatest percentage removal of Cu(II) was approximately 91.4 %, whereas Cd(II) removal was 88.1%. This result also demonstrated that maximum adsorption occurs after a certain dose of adsorbent, and hence the quantity of ions attached to the adsorbent and the number of free ions in the solution remains constant even though the adsorbent dose is raised. With increasing adsorbent dose in both cases, the removal percentage rises [19,20].

**Effect of contact time**

Since adsorption kinetics are dependent on the surface of the adsorbent, removal of Cu(II) and Cd(II) by KFC/CNT/PEG + Glu blend as a function of time was calculated. Cu(II) and Cd(II) ions uptake by KFC/CNT/PEG + Glu blend was investigated with increasing contact time, and the findings are presented in the figure 8. Due to the availability of greater
time for metal ions to form an attractive combination with the composite, efficiency increased as contact time increased. Initial removal occurred as soon as the metal and composite come into contact, and after a period of time, increasing the contact time did not boost uptake due to a decrease in readily available active sites for metal ion binding, and equilibrium was attained. This is significant since equilibrium time is one of the key criteria for a cost-effective wastewater treatment system.

![Figure 8: Effect of contact time](image)

**Effect of initial metal ion concentration**

The initial concentration of metal ions in the solution is critical in overcoming mass transfer barrier between the aqueous and solid phases (Dang et al., 2009). Figure 9 shows the effect of initial metal ion concentration on the adsorption of Cu(II) and Cd(II) onto KFC/CNT/PEG + Glu blend. The effect of initial metal ion concentration was investigated by altering it from 1000 to 50 mg/L while maintaining all other variables, such as time, pH, temperature, and absorbent dosage are kept constant. The percentage removal of each ion increases as the initial metal ion concentration decreases, as seen in Figure 9. The metal ions would engage with the binding sites at lower concentrations, facilitating approximately 100% adsorption, which can be attributed to the availability of unoccupied metal binding [21]. At higher concentration, due to the saturation of binding sites of biosorbents, more ions are left unadsorbed in the solution, reducing metal ion removal [22].
Adsorption isotherm

Various adsorption isotherm models have been used to optimise the design of an adsorption system and to explain adsorption equilibrium. The two commonly established Langmuir and Freundlich models for single solute systems were used in this study among the different adsorption isotherm models. The adsorption capacity and equilibrium coefficients for copper and cadmium ions from aqueous solution onto KFC/CNT/PEG + Glu adsorbents were investigated using these models.

The linearized form of the Langmuir isotherm model was given below

\[
\frac{C_{eq}}{C_{ads}} = \frac{b C_{eq}}{K_L} + \frac{1}{K_L}
\]

and

\[
C_{max} = \frac{K_L}{b}
\]

where,

- \(C_{ads}\) = amount of Cu(II)/Cd(II) adsorbed (mg/g)
- \(C_{eq}\) = equilibrium concentration of Cu(II)/Cd(II) in solution (mg/dm³)
- \(K_L\) (dm³/g) and \(b\) (dm³/mg) = Langmuir constant
- \(C_{max}\) = maximum Cu(II)/Cd(II) to adsorb onto 1 g of adsorbent (mg/g)

The plot of \(C_{eq}/C_{ads}\) vs \(C_{eq}\) yielded a straight line (Figure 10) confirming the favourability of Langmuir adsorption isotherm.

The linearized form of Freundlich equation was

\[
\log C_{ads} = \log K_F + \frac{1}{n} \log C_{eq}
\]

where,

- \(C_{ads}\) = amount of Cu(II)/Cd(II) adsorbed (mg/g)
- \(C_{eq}\) = equilibrium concentration of Cu(II)/Cd(II) in solution (mg/dm³)
From Figure 11 it was evident that the values of Freundlich constant can be calculated from the plot of log $C_{ads}$ vs log $C_{eq}$ and given in the Table 1.

**Table 1: Langmuir and Freundlich isotherm constants**

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Langmuir isotherm constants</th>
<th>Freundlich isotherm constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_L$ (dm$^3$/g)</td>
<td>$b$ (dm$^3$/mg)</td>
</tr>
<tr>
<td>Cd$^{2+}$ ion</td>
<td>0.9225</td>
<td>0.00876</td>
</tr>
<tr>
<td>Cu$^{2+}$ ion</td>
<td>1.2439</td>
<td>0.01128</td>
</tr>
</tbody>
</table>

The estimated Langmuir and Freundlich isotherm models based on the linear plots are shown in Table 1. From the results it was observed that, the Freundlich isotherm model was more favourable than Langmuir isotherm. Freundlich isotherm model ($R^2 = 0.9914$ for Cd(II) and 0.9665 for Cu(II) ions) had a higher $R^2$ value than Langmuir isotherm ($R^2 = 0.9162$ for Cd(II) and 0.8654 for Cu(II) ions), thus heterogeneous adsorption was more probable. The
ternary blend's $C_{\text{max}}$ value was found to be 105.26 mg/g for Cd(II) ion and 110.25 mg/g for Cu(II) ion.

**Kinetics studies**

The mechanism and rate of the desired adsorption process can be determined by looking at the kinetics of the adsorption process. To assess the results of the experiments, pseudo-first-order and pseudo-second-order kinetic models were used. The kinetics studies were conducted at a concentration of 200 ppm, a dosage of 1 g of adsorbent, and a pH of 5. The pseudo-first-order kinetics equation utilised was

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$$

The linearized pseudo-second-order kinetics equation used was

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e t}$$

where, $k_1$ and $k_2$ per min$^{-1}$ denotes first order and second order rate constant while $q_e$ (mg/g) and $q_t$ (mg/g) is relative adsorption quantity at equilibrium condition e and at time t (min) respectively. The plot of $t$ vs $\log (q_e - q_t)$ and $t$ vs $t/q_t$ gives the value of $k_1$, $k_2$ and $q_e$ from its slope and intercept respectively.

![Figure 12: Pseudo-first-order kinetics](image-url)
The pseudo-first-order and pseudo-second-order graphs of the KFC/CNT/PEG + Glu ternary blend were shown in figures 10 and 11, respectively, and the estimated parameters were provided in table 2. According to the determined $R^2$ value, the adsorption process follows pseudo-second-order kinetics ($0.9828$ for Cd(II) ion and $0.9965$ for Cu(II) ion) rather than pseudo-first-order kinetics ($0.8446$ for Cd(II) ion and $0.9693$ for Cu(II) ion).

### Table 2: Adsorption kinetic studies

<table>
<thead>
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<th>Metal ion</th>
<th>Pseudo-first order</th>
<th>Pseudo-second order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_e$ (mg/g)</td>
<td>$k_1$</td>
</tr>
<tr>
<td>Cd$^{2+}$ ion</td>
<td>427.27</td>
<td>0.01635</td>
</tr>
<tr>
<td>Cu$^{2+}$ ion</td>
<td>257.10</td>
<td>0.01244</td>
</tr>
</tbody>
</table>

Conclusion

In conclusion, utilising the sol-gel process, the unique KFC/CNT/PEG + Glu ternary blend was synthesised for the removal of Cu(II) and Cd(II) ions. FTIR, XRD, and SEM investigations were used to compare the results to pure KFC and KFC/CNT/PVA blend prepared without crosslinker. The rough surface area of KFC/CNT/PEG + Glu ternary blend with more number of voids was proved by XRD and SEM studies. A ternary blend of KFC/CNT/PVA + Glu was explored as an adsorbent for batch removal of Cu(II) and Cd(II) ions from aqueous solutions. The findings revealed that the generated ternary blend removes Cu(II) ions from aqueous solutions more effectively than Cd(II) ions, and that the sorption capacity is highly dependent on adsorption parameters. The Freundlich adsorption isotherm and pseudo-second order kinetics were more closely matched by the equilibrium data than by the Langmuir isotherm and pseudo-first order model.

References


